

SYNTHETIC MODIFICATION OF POLY(S-DVB) UNDER SOLVENT-FREE
CONDITIONS AT MILD TEMPERATURES TO INCORPORATE ADDITIONAL
MONOMERS

A THESIS

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE

MASTER OF SCIENCE

BY

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JULY 2018

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CHAPTER 1: BACKGROUND OF LITERATURE

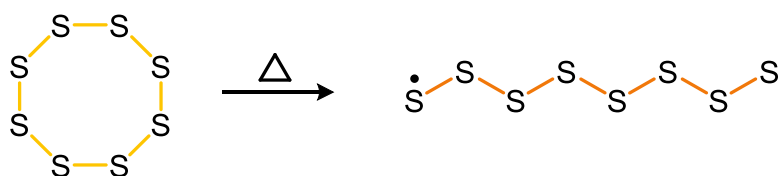
Elemental Sulfur and its Uses

Green chemistry is a large area of research that is growing due to the increase in environmental pollution and the need to counter that growth. Being able to recycle or repurpose materials that otherwise would not be used in a common setting is pivotal. Organosulfur compounds are common in the petroleum industry.¹ Most of the sulfur is removed from petroleum during hydrodesulfurization.² Hydrodesulfurization removes the sulfur from crude oil and reduces the possibility of sulfur dioxide emissions from the combustion of fossil fuels.³ Annually, ~60 million tons of sulfur are produced.⁴

Sulfur is not widely used as a reagent. It is used on a commercial scale for sulfuric acid production, phosphates for fertilizers, production of rubber, and smaller niche organic syntheses.⁵ Production of sulfuric acid (H_2SO_4) makes up 90% of all sulfur use in the United States.⁵ Despite these applications, sulfur is still in excess by millions of tons.³ Although sulfur is non-toxic overall, letting it sit in large mounds can have unknown consequences in the future. Being able to transform a static material, that is widely abundant and low in cost, to a dynamic one, is crucial.

Sulfur exists as a ring in nature. The common name, orthorhombic, is given to the structure which is an eight-membered ring. There are many different allotropes of sulfur but only three exist in a solid eight-membered ring. They are the α , β , and γ allotropes, and the most common one is the α -allotrope.⁶ The α -sulfur is found in nature as a green-yellow solid, and at 95 °C it turns into β -sulfur. Yellow powder collected in the large mounds at refineries is typically α -sulfur.⁶

Orthorhombic sulfur melts at $\sim 119\text{ }^{\circ}\text{C}$ and turns into a clear yellow liquid.⁶ At temperatures above $160\text{ }^{\circ}\text{C}$, the sulfur ring will break open to a sulfur chain with radicals on either end and change to an orange color as shown in Scheme 1.1. Sulfur will then begin to polymerize with itself and form an orange-red solid. Homo-polymerized sulfur is not stable and if allowed to cool down below $160\text{ }^{\circ}\text{C}$, the sulfur will revert to its most stable conformation and the yellow powder will reappear.



Scheme 1.1: Elemental Sulfur Ring Opening Above $160\text{ }^{\circ}\text{C}$

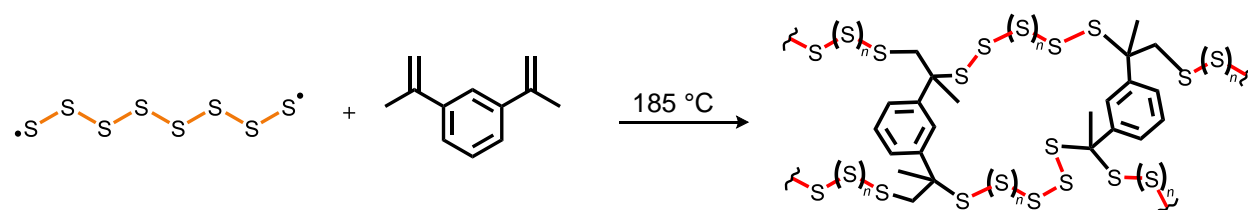
Sulfur's radical chemistry can aid in the cross-linking of other materials like rubber. Early rubber tires were prone to become very tacky during the summer and very hard and inelastic during the colder months.⁷ Charles Goodyear came about using sulfur and synthetic rubber by accident and discovered that sulfur can cross-link with polyisoprene chains in the polymer backbone under heat and pressure through a radical polymerization. The sulfur would strengthen the polyisoprene chains and the rubber would not be prone to extreme elasticity.⁷ The sulfur cross-linking from the radicals forms a ladder network and prevents the rubber from becoming tacky and unusable.

Sulfur can aid in polymerization of other materials as well such as using elemental sulfur and cyclic arylene disulfide oligomers to form very soluble polysulfides through radical polymerization.⁸ This allows the cross-linking of sulfur with the oligomers by hydrogen abstraction. The copolymerization type (solution or melt) was determined to play a role in the

molecular weight values.⁸ Solution-based copolymerization did not form polymers with high sulfur content due to the chain-ring equilibrium of sulfur. Melt copolymerizations did form high sulfur content polymers.⁸ Increased reaction time decreased the number of unreacted oligomers and free sulfur. The amount of free sulfur left after the reaction was detected by GPC for melt copolymerization.⁸ Sulfur rank is the amount of consecutive sulfur atoms in a row. This copolymerization with oligomers shows that sulfur can play a key role in polymer or materials chemistry due to its ability of cross-linking via hydrogen abstraction.

Inverse Vulcanization

Previous polymerizations with sulfur were done between an already formed polymer and elemental sulfur. In 2013 Jeffrey Pyun and his colleagues devised a new type of polymerization which they coined, “inverse vulcanization.” Inverse vulcanized polymers use elemental sulfur and another monomer to form a new polymer. Using elemental sulfur and 1,3-diisopropenylbenzene (DIB), Pyun was able to synthesize a polymer designated poly(sulfur-random-diisopropenylbenzene), [poly(S-*r*-DIB)].⁹ Scheme 1.2 shows the polymerization between elemental sulfur and DIB to form a general polymer matrix. The DIB monomer was able to stabilize the sulfur through cross-linking rather than it back-biting on itself and depolymerizing.



Scheme 1.2: Elemental Sulfur and DIB Forming Poly(S-DIB)

The chemistry that is involved with this polymerization is a derivative of a click-chemistry reaction (thiol-ene). When elemental sulfur is heated, the ring breaks apart and forms thiyl radicals.⁹ The radicals will then abstract a vinylic proton from the monomer and form a vinylic radical. This will generate a C-S bond when the radical interacts with a S-S bond. The thiyl radical can also bond to another alkene bond of another monomer and chain react to form a polymer.⁹ Not only does the sulfur polymerize with the monomer, but the monomers can also link together by the propagation of the radical to form C-C bonds.

Inverse vulcanization occurs at very high temperatures (>160 °C) to ensure the elemental sulfur ring breaks open allowing the polymerization to occur. The monomers that are incorporated need to be both high in boiling point and miscible with the sulfur which is one of the limitations of inverse vulcanization. The challenge, therefore, is to find some that are capable of both.

Inverse vulcanization is initiated upon the sulfur ring opening. Unlike typical radical polymerization, sulfur-sulfur bonds can then break apart even more into smaller pieces and bind to other monomers. These separate initiation events make it very challenging to control the reaction. This lack of control can lead to highly heterogenous samples with high polydispersities.

Research has been performed to try and control the process better using a reversible addition-fragmentation chain transfer (RAFT) polymerization agent.¹⁰ RAFT polymerization is the use of chain transfer agents to control the amount of propagation that occurs. This control of the chain length allows the polymer to have more uniform chain length. An increase in reaction time from a few minutes (free radical polymerization) to 6 hours with RAFT was observed. Better

control over the viscosity of the polymers and easier processability was obtained with this method.

A variety of monomers have been used for inverse vulcanization. The most common are cyclic aromatic compounds including DIB,⁹ divinylbenzene (DVB),¹¹ triisopropenylbenzene, (TIB),¹² and styrene,¹³ which are derivatives of one another. However, the presence and degree of cross-linking of each can differ which can affect the properties of the product. DIB is rather expensive whereas the cheaper version, DVB, is able to do the same type of polymerization and is actually quicker in terms of reaction/cure time (1-2 hours vs. 5-15 min respectively).⁹

Natural monomers have also been used for inverse vulcanization. Cardanol benzoxazines found in cashew nuts,¹⁴ *D*-limonene which is found in citrus fruit,¹⁵ and other sustainable monomers like terpenoids, and diallyl sulfides.⁵ Using naturally occurring monomers is another form of how inverse vulcanization is beneficial for environmental purposes by combining sustainable monomers with repurposed sulfur to form useful polymers.

Another class of monomers used in inverse vulcanization is benzoxazines. These monomers tend to have high temperature stability and can be modified with different functional groups for accelerated polymerizations. There is also no chance for the monomer to polymerize with itself.¹⁶

Most of the reported synthetic procedures for inverse vulcanization lack consistency. The use of inert gas, gradual increase in temperature over time,¹⁷ and curing post-polymerization⁹ have been recorded in the literature. The use of DVB has been prominent as a monomer for inverse vulcanization relative to others due to its low cost and similarity to DIB in structure. Multiple different procedures have been recorded for the formation of poly(S-DVB).

One method of poly(S-DVB) synthesis employs the use of an inert gas, argon, in a two-step synthesis. The elemental sulfur was added and heated at 185 °C until it turned into a cherry red color. DVB was added to the sulfur and the two monomers would mix together until the brittle solid was formed. No specific time-scale given for their syntheses. For polymers with higher amounts of DVB, the reaction would run until the material reached a viscous state. For both brittle and viscous samples, the reactions were quenched using liquid N₂ to break the solid block of material. The samples were then cured in an oven for 3 hours at 120 °C to change samples into a hard, transparent polymer.¹¹

In another case, two polymers using bismaleimide (BMI), poly(S-BMI) and poly(S-DVB-BMI), were synthesized in a two-step reaction at 185 °C based off the Pyun synthesis. Once elemental sulfur had polymerized, the monomers were added to the oligomeric sulfur and allowed to react for five minutes then cooled down to room temperature. Poly(S-BMI) and poly(S-DVB-BMI) were then allowed to react for 30 minutes at 180 °C. Lower sulfur contents (20-40%) were used to form the poly(S-BMI) and the higher sulfur contents (70-90%) were used to form the poly(S-DVB-BMI) terpolymer. Furthermore, the polymers were all cooled down to room temperature rather than using liquid N₂ to quench the reaction.¹⁷

Another variation to the technique devised a synthesis under pressure. Sulfur and DVB were added together on a 200-g scale in a polytetrafluoroethylene (PTFE)-inlay. DVB was added with the sulfur at 10-35% wt. using 5% wt. increments for various ratios of sulfur and DVB. The system was then enclosed under pressure and allowed to react at a temperature of 160 °C for 90 minutes. After the reaction time, the samples were then pulverized into a powder for use in characterization.²

Almost all the poly(S-DVB) inverse vulcanization procedures lack consistency which points to the versatility of this type of polymerization. Not only does the formation of poly(S-DVB) change, but all the different monomers used have a specific synthesis. Slight modifications can be made to the procedure to tailor a polymer for a role in various applications.

Applications of Inverse Vulcanized Materials

Employing different monomers forms various types of polysulfides that are synthesized to fit a specific role. Currently the applications of inverse vulcanized polymers are a very small niche in Li-S battery cathode material and healable infrared optical materials research. The electrochemical potential and refractive index of polymeric sulfur has led to a substantial amount of research in these two areas. There are other less researched applications in molding, processing, stimuli-response to nanoparticles, and metal capture.

Li-S batteries have been studied because of their ability to be more effective than other batteries like lead-acid, or Li-ion batteries in terms of their specific energy.¹⁰ Current cathodes being used are not nearly as reliable as many had hoped. There are issues with short lifetimes and material degradation. Previously, elemental sulfur has been used as a cathode. Sulfur-based cathodes have a capacity of 1672 mAh/g and a specific energy of 2600 Wh/kg.¹⁰ However, they are very unstable and can often decrease the lifetime of the battery.^{10,14} Another issue is that over time the presence of solid deposits will form on the cathode using a sulfur-based cathode. These deposits are comprised of higher order sulfides like Li_2S_2 , Li_2S_4 , and Li_2S_6 through the reduction of Li_2S .^{14,18,19} Once they build up over time, the usefulness of the battery diminishes.

The battery life is measured in charge/discharge cycles and shows a drastic decrease in cycle amount using a sulfur-based cathode.

Polysulfides were then used as cathodes to study their effect on a battery's lifetime and reliability. Inverse vulcanization has demonstrated stability over a period of months using poly(S-*r*-DIB).³ This idea was then put to work using various polysulfides. The use of benzoxazines, DVB, and other monomers showed similar outcomes in terms of their capacitance and stability. Cathodes made from polysulfides show a decrease in charge/discharge cycles over time but show a substantial increase in cycle amounts. Some polysulfides achieved over 1000 cycles while using styrene monomer.¹³ In the presence of a polysulfide with cardanol benzoxazine monomer, the solid sulfide deposit formation was greatly diminished.^{13,14} Furthermore, the increase of organic content in the polysulfide greatly reduces the capacitance of the battery.¹⁴ This suggests that the higher order sulfur polysulfides are able to function more effectively due to the amount of sulfur in the polymer.

Optical Materials

Polymerized sulfur has a high refractive index (RI). Research of IR optical materials using inverse vulcanized materials is supported as they exhibit transparent properties in the infrared. This enables them to be used in thermal imaging.²⁰ Most organic polymeric materials have low RI (1.5-1.6) and absorb in the IR spectrum due to the C-H bonds.¹² The ability to achieve a high RI is very challenging. Some inorganic materials can exhibit high RI signals between 2-5.²¹ The issue with these materials is their high cost. Sulfur-based polymers offer a low-cost alternative to inorganic materials and still have a high RI. Poly(S-*r*-DIB) demonstrated the highest RI signal yet

found in an organic polymer (1.75-1.85). Materials with high RI typically show high transparency in the IR region.¹²

The transparency of inverse vulcanized polymers was researched, and the results were compared to other standard lenses. Zinc selenide and germanium lenses, typical lenses used in lasers, are very fragile. If they are scratched, or damaged naturally in any way, they are rendered useless and need replacement.²² It would be ideal to use a material after it has been damaged, and still retain its effectiveness.

Healable materials are a largely growing field. Some healable materials require dynamic covalent bonds.²² Disulfide bonds are dynamic as they are responsive to light, heat, and mechanical force. Poly(*S-r*-DIB) polymers are transparent and IR active.²² Upon any sort of damage, poly(*S-r*-DIB) can be healed to their initial state unlike the inorganic lenses. The application of heat at 100 °C can heal any scratch, dent, or other defect due to the reorganization of the dynamic S-S bonds in the polymer. These materials can even be healed after cleaving the lens in two and placing the two pieces together and heating the pieces.

Another area being researched is incorporating nanoparticles with inverse vulcanized polymers such as poly(*S-r*-DIB). The goal is to determine if this material can alter the optical properties. Current research has shown that Au nanoparticles, FeO nanoparticles, and quantum dots can be incorporated into poly(*S-r*-DIB) and exhibit color changes specific to whatever nanoparticle is present in the matrix.²³ The colors can range from rust-orange, red-black, and red-orange respectively.²³ The ability of these nanoparticle-infused polysulfides to increase the IR properties remains to be seen. Using polysulfides as optical lenses has a very high potential for

future use in defense applications. This could include aircraft instrumentation, optics for shoulder-fired weaponry, and even helmet heads-up displays for ground troops.

Capture of Toxic Metal Ions in Water

Metal ions can be found in water; however, the presence of certain heavy metal ions can be extremely toxic to human health. Metal remediation of toxic metal ions is always being researched for more efficient methods. Using extraction techniques to remove the ions from water, soil, etc. is important for the environment and humans alike.²⁴ Mercury is a very dangerous metal ion. Finding a material that captures mercury at large concentrations in a short amount of time is very challenging. However, sulfur has a high affinity for mercury and polysulfides have plenty of sulfur available for binding. Polysulfides such as poly(*S-r*-DIB) and poly(*S-r*-limonene) have been tested to determine how effective they are at mercury binding.^{15,25} Poly(*S-r*-limonene) was shown to bind to mercury effectively. Even more interesting is that poly(*S-r*-limonene) underwent a color change from a dark red to a light yellow indicating the presence of the mercury. The stimuli responsive nature of the polymer is very promising for further mercury binding applications. The polysulfide was inconclusive regarding binding to other metal ions like iron, copper, calcium, etc. Metal remediation techniques were performed using poly(*S-r*-limonene) and pond water. They were effective because the yellow solid formed in the presence of mercury was still attached to the polysulfide even after washing with water to remove the silt and pond residue.¹⁵

Poly(*S-r*-DIB) shows mercury binding abilities as well. Using this polysulfide, the mercury binding was very minimal. SEM images showed a small pore size which would limit metal ion

transport through the polymer network.²⁵ For the metal ions to be more effectively bound to the polysulfide, the surface area would need to be increased. Using supercritical CO₂, the pores increased greatly in size and appeared like a foam. Mercury ions could be captured much more rapidly and at much greater concentrations when poly(S-DIB) pore size was increased. Since these materials would likely be used in a system where the water is constantly moving, they were used in a flow test. Poly(S-*r*-DIB) was found to be very effective at binding to mercury under a foamed state.²⁵

Inverse vulcanized polymers offer cheaper alternatives to many functional materials. This includes using polysulfides as cathodes, metal capturing materials, IR transparent optical lenses for possible electronics and defense purposes, and mercury detectors. These applications provide an opportunity for further improvement and eventually their use in commercial applications.

Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs)

Inverse vulcanization utilizes large amounts of elemental sulfur and another monomer to form a new polymer. This method combines sulfur and monomer above 160 °C. The sulfur ring breaks open and reacts with the monomer. A leading drawback to this process is the lack of different monomers used. Typical reaction temperatures take place around 180 °C and even higher in certain cases. This high temperature can limit the use of different monomers as many do not have boiling points above 160 °C. The challenge is to determine a route in which many different monomers can be utilized rather than a select few. They also need to be miscible with the polymer being used which also presents an issue.

The idea of including an additional monomer has only recently been researched using poly(*S-r-Sty*) and acrylate monomers to form terpolymers poly(*S-r-Sty-r-ODA*). Octadecyl acrylate (ODA) is a monofunctional monomer.²⁶ The main goal was to improve the miscibility of allylic acrylates since they were not miscible with elemental sulfur. However, they could be miscible with poly(*S-r-Sty*) and were easy to synthesize. They were able to synthesize terpolymers with an additional monomer that was not previously used which opens the possibility for other miscible monomers in terpolymer synthesis. The temperatures being used are lower than the initial inverse vulcanization temperature, but still relatively high (110-170 °C).²⁶

Purpose

The main goal was to use poly(*S-DVB*) to initiate polymerization with other monomers at lower temperatures than previously used. The lower temperature can initiate polymerization as linear S-S bonds will cleave between 80-100 °C. This cleaving allows sulfur radicals to reform and can incorporate an additional monomer into poly(*S-r-DVB*) without the aid of solvent. Using poly(*S-r-DVB*) the challenge was finding a monomer that had a high enough boiling point at least above 80 °C. A family of monomers with similar structure and with different reactive groups (vinyl, allyl, monofunctional and difunctional) was chosen for the project. The effects on the polymer structure and physical properties by adding the additional monomer was studied.

CHAPTER 2: METHODS

Materials

All materials were used without further purification. Elemental sulfur (99.5%-100.5%), 1,4-cyclohexanedimethanol divinyl ether (98%, mix of isomers), and allyl ether (98%) were commercially obtained from Sigma-Aldrich. Cyclohexyl vinyl ether (95%) was obtained from Acros. Divinylbenzene (80%, mix of isomers w/ ethylvinyl benzene) was obtained from Alfa-Aesar. Cyclohexyl allyl ether was synthesized and confirmed via NMR and GC/MS according to literature (Appendix Figures 5.1 and 5.2).²⁷

Poly(*S-r*-DVB) Formation

Formation of poly(*S-r*-DVB) is prepared using the combination of elemental sulfur and divinylbenzene (DVB). DVB has been chosen as the monomer due to its lower cost and ability to polymerize readily with the elemental sulfur via inverse vulcanization. Various amounts of sulfur, 30-90% by weight, were measured out to the corresponding DVB percentages (70-10% respectively). A typical synthesis for 50% sulfur poly(*S*-DVB) would be 0.5 g S₈ with 0.5 g of DVB combined in a vial and heated at 185 °C for 30 minutes.³ The 30-min time scale is used to prevent the degradation of the polymer at such a high temperature. This timescale also provided the highest molecular weights. Any increase in time can cause the polymer to break apart and the sulfur chains can reform their stable eight-membered ring. Upon removing the vial from the bath, the sample was immediately cooled in liquid nitrogen. The vial was broken open and the sample cleanly removed.

Synthesis of all polymers took place in a temperature controlled mineral oil bath while seated in a vial holder (Figure 2.1). The holder was designed to hold eight samples (screw-thread 1-dram vials) at one time. Production of the vial holder was done using a mill and various specialized metal-drilling equipment.



Figure 2.1: Glass Vial Holder

Synthesis of Poly(S-DVB): Additional Monomer and Controls

The poly(S-*r*-DVB) from the initial synthesis was broken apart into small pieces for larger surface area interaction with an additional monomer. Using the crushed poly(S-*r*-DVB), the material was weighed out with an additional monomer, 1,4-cyclohexanedimethanol divinylether (CDE). Various ratios of poly(S-*r*-DVB):CDE (w/w) are weighed out (100:1 – 1:100). The ratios 100:1, 50:1, and 10:1 are prepared using only poly(S_{50%}-*r*-DVB_{50%}). All other ratios of CDE were also reacted with poly(S-DVB) of varied sulfur contents (30-90% sulfur). This reaction is carried out on a 600-mg scale without the use of solvents. For the 1:1 ratio of poly(S-DVB):CDE, a typical synthesis involves combining 300 mg of crushed poly(S-DVB) and 300 mg of CDE. The vial is placed in an oil bath at 90 °C for 24 hours. The vial is then removed and allowed to cool to room temperature.

The poly(S-DVB) and the additional monomer need to be fully mixed with one another to react. Dimethylformamide (DMF) was added to increase the incorporation of the prepolymer and

the additional monomer. The boiling point of DMF was well above the reaction temperature of 90 °C. The scale of poly(S-*r*-DVB), CDE is 0.6 g in 0.5 mL of DMF. The amount of DMF added is held constant for all ratios. The solution is then heated for 24 hours at 90 °C.

The polymer was precipitated out of solution using cold methanol. Any remaining unreacted monomer will be decanted out with the methanol. The polymer is dried on the rotary-evaporator to remove any remaining methanol. The resulting material is dissolved with a minimal amount of DCM and then precipitated again with cold methanol. The precipitation steps are repeated until clear supernatant is observed. The flask is placed on a vacuum line for 24 hours.

Poly(S-DVB-AE), poly(S-DVB-CAE), and poly(S-DVB-CVE) were formed by using crushed poly(S-DVB) and additional monomer (AE, CAE, CVE) in a vial at a 600 mg scale. The prepolymer and additional monomer were heated at 90 °C for 4 days. After heating, they were removed from the oil bath and were cooled to room temperature.

A control reaction was conducted by reheating 600 mg of 50% sulfur poly(S-DVB) at 90 °C for 24 hours. After heating, the vial was removed from the oil bath and cooled to room temperature. The 1:1 poly(S-DVB):DVB control was prepared by combining 300 mg of 50% sulfur poly(S-DVB) and 300 mg of DVB in a vial with a stir bar. The vial was heated for 3 days at 90 °C, removed from the oil bath, and allowed to cool to room temperature.

Polymer Characterization

¹H-NMR was performed on all polymers samples with a JEOL spectrometer coupled with an Oxford 400 MHz magnet. Sample preparation was done by dissolving the polymer in CDCl₃. Polymer solutions were filtered through cotton into the NMR tube to eliminate any undissolved

material from entering the tube. 16 scans were collected for each sample and the resulting spectra analyzed for propagation, HC-S bonding, and remaining unreacted monomer.

Gel permeation chromatography was performed using an Agilent GPC, with dichloromethane (DCM) solvent and PolyPore 300x7.5 mm columns (Part no. PL1113-6500). To calibrate the GPC, polystyrene standards with molecular weights ranging from 202,100 g/mol to 1440 g/mol were measured out and dissolved in DCM at 1 mg/mL. The calibration sample is run through the GPC to create a calibration curve. Samples were weighed out to approximately 150 mg with 2 mL of DCM for consistency. Molecular weights and the polydispersity were determined from integration of the elution peak(s) with a polystyrene calibration curve.

DSC was conducted using a Perkin Elmer Pyris 1 instrument with a 2P Intracooler. Samples were prepared by weighing out 40-50 mg samples to ensure the detection of the glass transition temperature. Polymers were analyzed from -50 °C to 160 °C at a scan rate of 10 °C/min

Metal Binding Using Poly(S-DVB-CDE)

Various metal solutions of concentration, 2.45×10^{-4} M, were prepared using $\text{FeCl}_2 \bullet 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \bullet 2\text{H}_2\text{O}$ salts and distilled water. Poly(S-*r*-DVB-CDE) was cut down to small pieces for increased surface area. The material was placed in a glass vial with 10 mL of the aqueous metal solution and allowed to soak in the solution for 24 hours. The polymer samples were removed from the vials and then the remaining solution was analyzed to determine the metal ion concentration remaining. A control of each metal ion was conducted by placing 10 mL of the metal solution in a vial without the polymer and testing for 24 hours. This was to ensure that only samples were capturing metal ions and not the vial walls.

Flame AA analysis was completed using a Perkin Elmer AAnalyst 100 spectrometer to determine the absorbance of each solution. The absorbance values would be compared to five standard solution absorbance values on a line graph provided by the AAnalyst software. The solutions were prepared by diluting the starting concentration 2.45×10^{-4} M to 1.22×10^{-4} M, 6.13×10^{-5} M, 3.06×10^{-5} M, and 1.53×10^{-5} M. The polymer was removed from the aqueous metal solutions. The remaining solution was analyzed for the metal concentration at a suction rate of 10 mL/min. The concentration of the polymer-exposed solution was found by extrapolating the value on a standard calibration curve. The absorbance value was then used to calculate the final concentration relative to the starting concentration standard.

Solubility Testing

Solubility of all polymers was tested in DCM solvent. Each polymer was weighed out to approximately 150 mg and 2 mL of DCM was placed in the pre-weighed vials. The samples were allowed to dissolve for 8 hours. The dissolved polymer solution was pipetted out of the vial and the remaining solid allowed to dry in the oven for 10 minutes. The dried vials were removed from the oven and allowed to cool to room temperature. The vial was then weighed, and the final and initial weights were used to calculate the remaining undissolved polymer.

Swelling

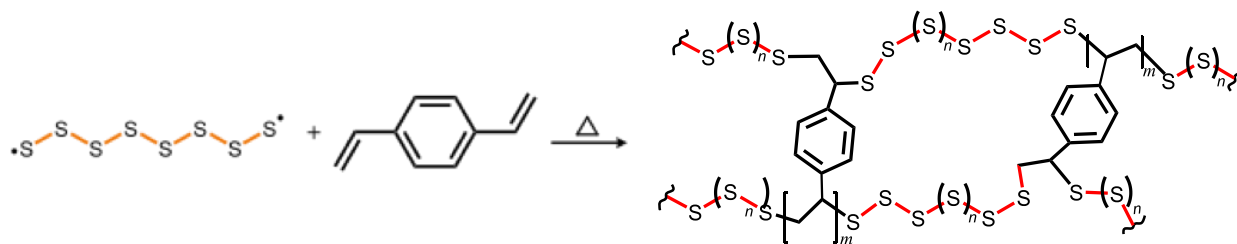
Swelling was necessary to determine how CDE might affect the metal capturing ability of a polysulfide by allowing metal ions to travel through the polymer matrix. All polymer swelling capabilities were determined by placing a small polymer disc in 2 mL of distilled water. The

samples being tested were cut out approximately to a similar size using a cutting press (~ 7 mm diameter, ~ 3 mm depth). Average weight for each poly(S-DVB-CDE) used was about 73 mg. Initial weights of the samples were recorded and then allowed to soak in 2 mL of deionized water for 24 hours. They were dried off briefly in a paper towel and immediately were weighed. The difference of the two weights (final-initial) was calculated and then divided by the initial weight to determine what percentage the sample swelled in the water.

CHAPTER 3: RESULTS

Poly(S-r-DVB) Synthesis

Poly(S-DVB) is formed by using elemental sulfur and divinylbenzene (DVB). Sulfur contents were varied (30-90%) as well as the corresponding DVB content (70-10%). Both are combined in a glass vial with a stir bar and allowed to mix at 185 °C for 30 minutes. Scheme 3.1 shows the general reaction.



Scheme 3.1 Elemental Sulfur and DVB Forming Poly(S-DVB)

Elemental sulfur and DVB undergo a color change as poly(S-DVB) is formed. The yellow sulfur powder melts into a yellow liquid and begins to interact with DVB, (Figure 3.1 A). Further heating resulted in a reddish-orange color indicating the sulfur ring opening and radical formation initiating the polymerization with DVB (Figure 3.1 B). Around 1.5 minutes, the polymer began to solidify. The stir bar stopped rotating, and the solid showed a rapid color change from reddish-orange to a reddish black color (Figure 3.1 C). Some samples began bubbling slightly from either the formation of a gas or boiling monomer which resulted from the autocatalytic effect (Figure 3.1 D). At about 2 minutes the solid now had reached a stage of full solidification and no more bubbling occurs.

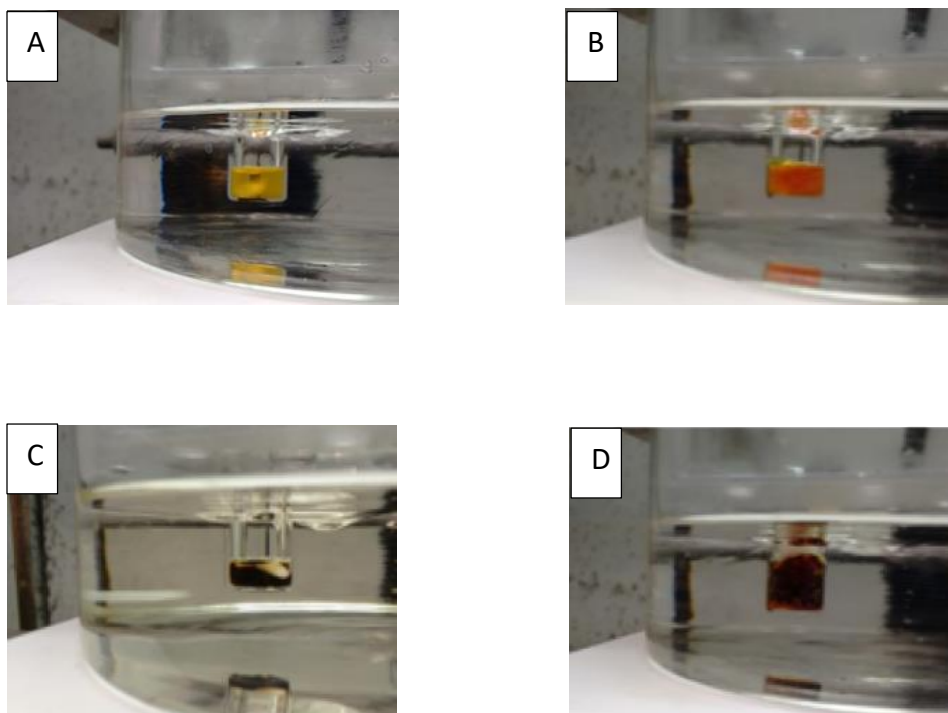


Figure 3.1 Reaction Progression of Elemental Sulfur and DVB

The autocatalytic effect is caused by the increase in viscosity of the polymer matrix. The high viscosity reduces the amount of termination while the monomer polymerizes at a rapid rate causing a substantial release of energy.²⁸ This can affect the physical properties of the polymer.

The general reaction happens very quickly and undergoes the same stages of sulfur melting, sulfur radical formation, and solidification of the polymer every time. However, the autocatalytic effect only occurs in the mid-range of sulfur percentages (40-60% sulfur). The scale of the reaction can affect if the autocatalytic effect occurs as well. All data presented is with a 1.0 g scale of sulfur and DVB for the sulfur poly(S-DVB). The 0.5 g scale was tried, and the autocatalytic effect was rarely observed at that scale.

Once the 30-minute reaction time was completed, the samples were immediately placed in liquid nitrogen to quench the reaction. The rapid cooling with liquid nitrogen also enabled the complete retrieval of all the material from the vial. This was not possible with samples cooled at

room temperature as they would stick to the vial walls. Liquid nitrogen made the crushing of the samples much easier and offered more surface interaction for later syntheses. Formation of a gas was also noticed as hissing sound escaped the vial upon opening and an odor was detected, so samples were kept under the hood. The gas was prevalent in the mid-range sulfur content poly(S-DVB).

^1H -NMR of Poly(S-DVB)

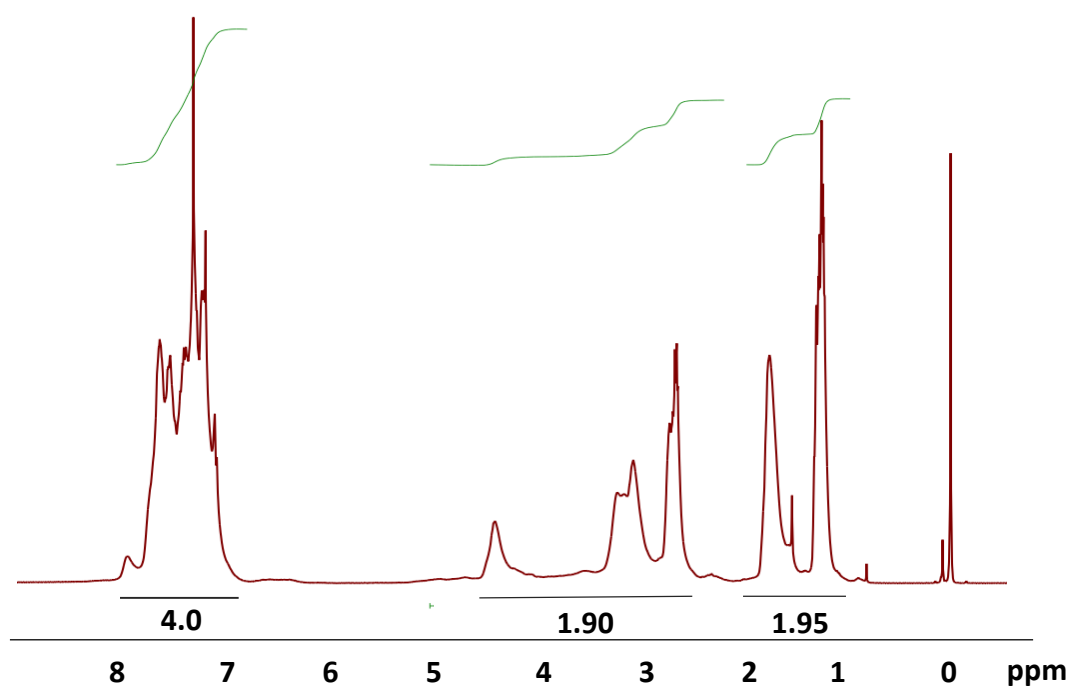


Figure 3.2 ^1H -NMR of Poly(S_{50%}-DVB_{50%})

Figure 3.2 shows the ^1H -NMR spectrum of poly(S_{50%}-DVB_{50%}). The CDCl_3 peak showing up at 7.26 ppm does overlap with the aromatic protons of DVB and is included in the integration. The integration of the entire aromatic region is considered to be from DVB. Other solvents like DMSO were not used as the water peak would appear at 3.33 ppm which would interfere with

the integration of the HC-S peaks. The indication that DVB has been polymerized can be observed by the disappearance of the alkene protons in the 5-6 ppm region and the appearance of peaks in the 1-2 and 3-5 ppm range.

The 1-2 ppm region is where propagation occurs (HC-C bonding). Peaks from HC-S appear in the 3-5 ppm regions. Integration of these peaks show that a ratio of HC-C:HC-S is $\sim 1.0:1.0$. This indicates that there is an equal amount of each in the 50% sulfur poly(S-DVB). $^1\text{H-NMR}$ spectra of poly(S_{30%}-DVB_{70%}) and poly(S_{70%}-DVB_{30%}) can be found in the appendix (Figures 5.3 and 5.4). The peak locations of the various sulfur contents do not change. However, the HC-C:HC-S bond ratios do change. The 30 and 70% sulfur poly(S-DVB) show an increase in HC-C bonding (1.68 and 4.21 respectively) compared to the 50% sulfur (1.0).

Solubility and GPC of Poly(S-DVB)

The solubility of poly(S-DVB) was tested in dichloromethane (DCM). When poly(S-DVB) is dissolved at 75 mg/mL in DCM, there is a definitive color change as the sulfur to DVB ratio is altered shown in Figure 3.3. Poly(S_{30%}-DVB_{70%}) is less dense than DCM unlike the other samples. Poly(S_{30%}-DVB_{70%}) has a larger amount of DVB (less dense than DCM) incorporated into the polymer. There is low polymer solubility at 30% sulfur because of the high amount of DVB cross-linking forming a gel-like network. For polymers with mid-range sulfur content (40-50%), the solubility is very high. Once higher ranges of sulfur are reached (60-90%), the solubility decreases rapidly due to sulfur's insolubility. Figure 3.3 B depicts the quantitative solubility data for poly(S-DVB). The graph shows the drastic changes in solubility by varying the sulfur content.

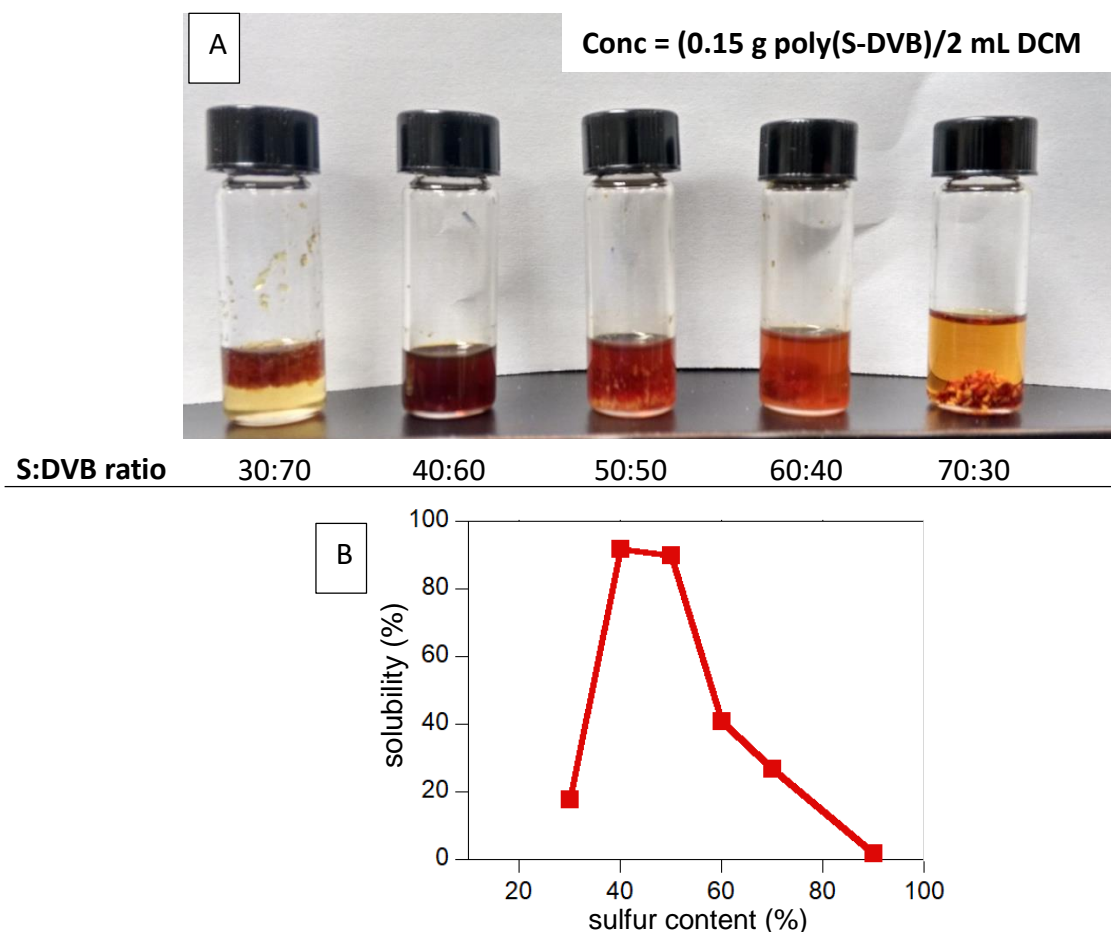


Figure 3.3: (A) Image and (B) Graph Depicting the Solubility of Poly(S-DVB) with Various Sulfur Contents

Gel permeation chromatography (GPC) was performed to determine the molecular weight of all poly(S-DVB) samples. The data shows a slight increase in the molecular weight up to 3700 g/mol as sulfur content increases from 30 to 50% sulfur, then drops down to 1,800 g/mol with 60% sulfur (Table 3.1). The elution peaks for poly(S-DVB) are very jagged and not uniform which is the result of the low molecular weight chains in poly(S-DVB) as well as reaching the limits of the GPC columns for detection of molecular weight. For controlled polymerizations GPC would exhibit one smooth peak and would have a polydispersity index (PDI) closer to 1.0. The PDI indicates the amount of chain length variation that is in the sample being analyzed. In

comparison, inverse vulcanization is a very uncontrolled polymerization and PDI values are typically greater than 2.0.

Table 3.1 GPC Data of Poly(S-DVB)

S-DVB	M_n (g/mol)	M_w (g/mol)	PDI
30-70	1100	2700	2.5
40-60	1200	2300	1.9
50-50	1400	3700	2.7
60-40	1100	1800	1.7

The highest molecular weight reached is the 50% sulfur content at 3700 g/mol. On both ends of the spectrum, the polymers are not as soluble due to the cross-linking of monomer in the case of the 30% sulfur poly(S-DVB) and the high sulfur content in the 70% sulfur poly(S-DVB). The relationship between solubility and molecular weight is not direct. However, if the sample is more soluble the molecular weight given is a better overall picture of the sample. The GPC elution scans show differences in intensity of each sample either due to the refractive index of each sample or solubility (Appendix Figure 5.5). All the sulfur contents besides 30% sulfur poly(S-DVB) are more intense likely due to low solubility of the sample.

DSC and Qualitative Properties of Poly(S-DVB)

Qualitatively, poly(S-DVB) changes as the sulfur contents vary. The lower end of the sulfur spectrum creates a light orange, very brittle solid. The solid can be broken apart by hand and is homogenous and glassy throughout. The edges are smooth at the fracture points. The 40-50%

sulfur poly(S-DVB) polymers appear to become more like a taffy. The material that clings to the vial wall in this range of sulfur tends to be slightly more brittle compared to the middle where it is much softer. The cause of the various sections of 40 and 50% sulfur poly(S-DVB) has not been investigated. Higher sulfur contents such as 90%, form a polymer that resists deformation. This is observed when squeezing the 90% sulfur poly(S-DVB) between two fingers. Upon releasing pressure, the material reverts to its original shape.

Differential scanning calorimetry (DSC) was performed to determine the glass transition temperatures (T_g) of all poly(S-DVB) samples. The polymers that are being formed during inverse vulcanization are not crystalline in structure, so they do not have a melting point much like other non-polymeric compounds. Instead they are amorphous solids. Samples were heated from -50 to 160 °C, cooled at 20 °C per minute and heated again. Using a double scan for the samples ensures the cooling rate of the samples is held constant and that they have the same thermal history. The thermograms in Figure 3.4 are used to determine the T_g . The small dip in the graph shows a temperature range approximately where the polymer chains begin to freely move past one another. As a reference point, elemental sulfur's melting point occurs at 119 °C. The large dip in the orange scan shows that sulfur is remaining in the sample. Sometimes, the elemental sulfur that showed up in the first scan no longer appears in the second scan indicating that the sulfur that initially was unreacted is no longer present in the sample. This suggests that the sulfur could incorporate successfully after the heat was applied to the sample during the first scan.

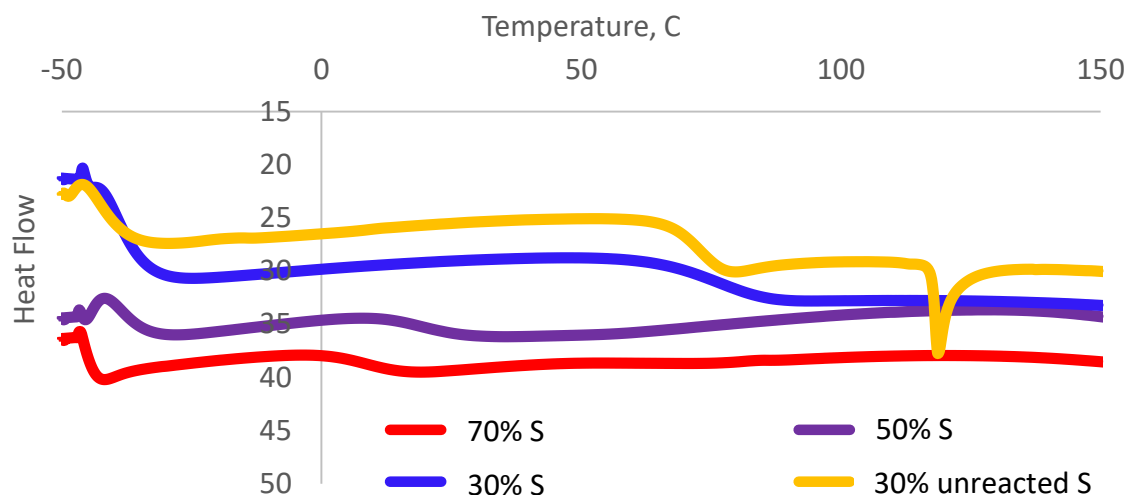
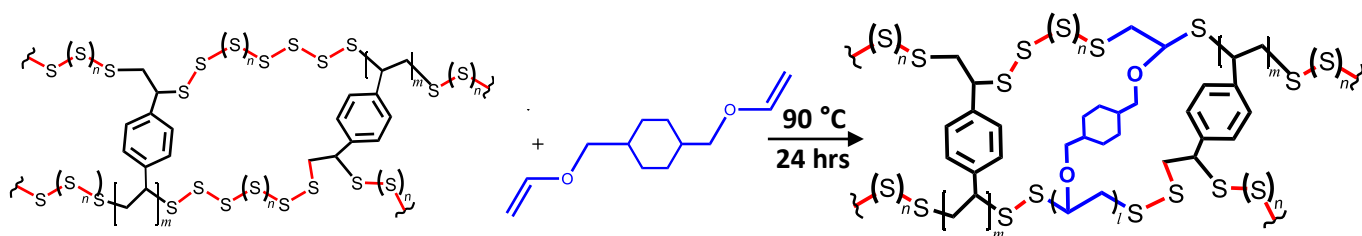


Figure 3.4 Thermograms of Poly(S-DVB) with Various Sulfur Content

As the sulfur content increases, the T_g decreases: 30% sulfur ~ 74 °C (blue), 50% sulfur ~ 52 °C (purple), and 70% sulfur ~ 28 °C (red). Higher sulfur contents decrease the T_g because of the decrease in cross-linking. The cross-linking decreases the amount of free volume that the polymer chains have. The monomer, DVB, has a benzene ring and in large quantities creates a matrix that has a smaller free volume. This decrease in free volume increases T_g of samples because of the resistance of chain movement.

Terpolymer Synthesis

Starting with crushed poly(S-DVB) for better surface area interaction, 1,4-cyclohexanedimethanol divinyl ether (CDE), was added solvent-free and reacted at 90 °C to form a terpolymer. The formation of poly(S-DVB-CDE) is shown in Scheme 3.2. Different ratios of poly(S-DVB):CDE were formed (1:1-1:100) for all sulfur contents.



Scheme 3.2 Synthesis of Poly(S-DVB-CDE)

The resulting poly(S-DVB-CDE) shows a change to the polymer appearance relative to poly(S-DVB). The starting material, poly(S-DVB), is transparent for the 30% sulfur content. The 50-90% sulfur poly(S-DVB) are very opaque. When CDE is incorporated, the opaque polymer changes from a dark brownish black into a mocha brown material. The mocha color is only observed in the 50% sulfur poly(S-DVB):CDE (1:1) ratio. Samples with higher CDE content, poly(S-DVB):CDE ratios (1:10-1:100) with 50% sulfur have a brown-black to black color. There is a noticeable change in color from the initial material which is a red-brown material. For poly(S-DVB-CDE) with other sulfur contents, no large color change is observed. The reason for the noticeable color change only for the 1:1 50% sulfur poly(S-DVB):CDE is still not well understood.

¹H-NMR of poly(S-DVB-CDE)

CDE is different than DVB in several ways spectroscopically. The vinylic protons of DVB show up between 5-6 ppm. CDE's alkene protons appear at 6.5 ppm and 4.1-4.3 ppm. This shift up-field is due to the oxygen heteroatom included in CDE. Furthermore, in DVB, there are no protons from 1-2 ppm. Once polymerized, however, protons adjacent to HC-C bonds appear in this range. Cyclohexane protons show up in the 1-2 ppm range. Overlapping with peaks in the poly(S-DVB) creates a problem when determining just how much CDE has been successfully incorporated. However, another verification of polymerization is if the double bond peaks of CDE

are no longer observed in the NMR after the reaction has taken place. In the case of the NMR spectrum below, Figure 3.5, the double bond protons of CDE are no longer visible. This supports the complete consumption of CDE.

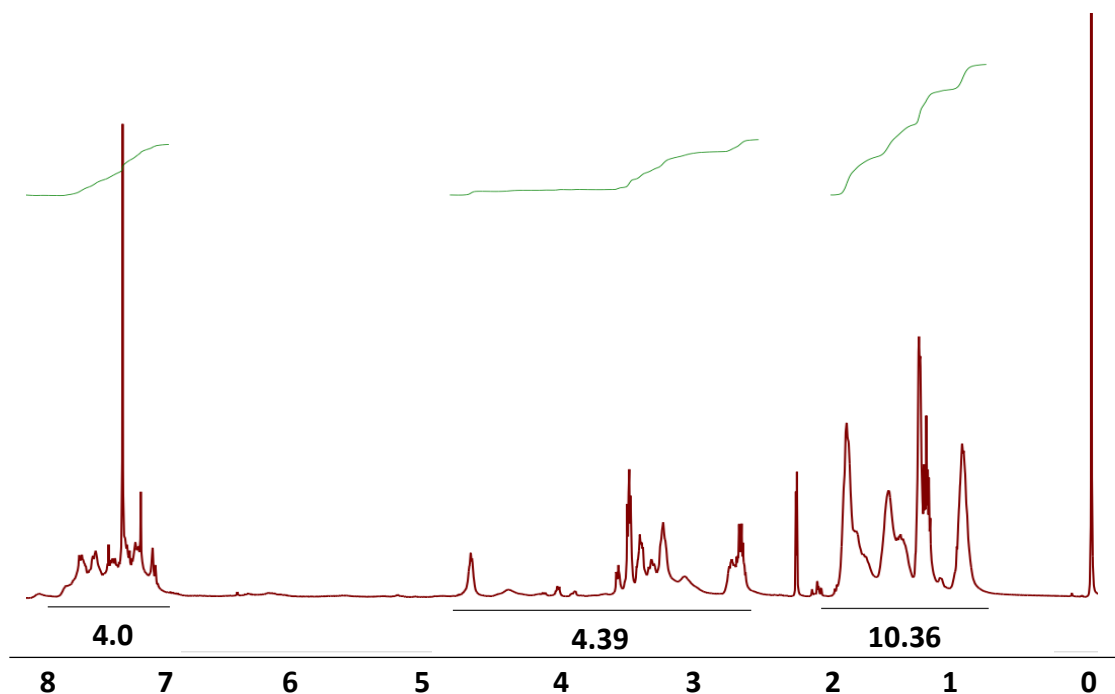


Figure 3.5 ^1H -NMR of Poly(S-DVB-CDE)

In order to analyze how CDE was being incorporated into the polymer matrix (CDE-S bond, or CDE-another monomer bonding) the ratio of HC-S:HC-C bonding was determined by using the integrated values of the NMR spectra. Calculations were performed for the various ratios of poly(S-DVB):CDE to determine how many protons were from the alkene protons of CDE by subtracting its ether and cyclohexane protons. The samples showed an increase in HC-C bonding relative to the HC-S bonding for all sulfur contents tested as CDE is added. The reason for the increase in HC-C bonding may be due to the high amount of additional monomer relative to the

sulfur present in the sample. This would allow propagation of the radical across more monomer units rather than from sulfur to monomer to another sulfur unit.

Controls of 30, 50, and 70% sulfur poly(S-DVB) were tested by reheating the material for 24 hours at 90 °C. The controls were tested to determine how the reheating would affect the HC-S:HC-C bonding, if at all. The ^1H -NMR results showed that reheated 30% sulfur poly(S-DVB)'s HC-C bonding (1.6) shows no substantial change from the initial 30% sulfur poly(S-DVB), (1.7). The reheated 50% sulfur poly(S-DVB)'s HC-C bonding (1.3) showed a slight increase from the initial 50% sulfur poly(S-DVB), (1.0), and the reheated 70% sulfur poly(S-DVB) showed a decrease in HC-C bonding (1.5) compared to the initial 70% sulfur poly(S-DVB), (4.2). The initial HC-C bond value of 4.2 for 70% sulfur could be the cause of solubility and not representative of the actual value.

Another control using 50% sulfur poly(S-DVB) was also tested by adding more DVB. This was done to investigate the effect the additional monomer had on the HC-S:HC-C ratio. Figure 3.6 shows the ^1H -NMR of poly(S-DVB):DVB at a 1:1 ratio. There is an increase of HC-C bonding (1.7) compared to the starting material (1.0). This increase in HC-C bonding is from the addition of more monomer since there is a limited amount of sulfur radicals to incorporate with to form HC-S bonds. There is still residual DVB in the polymer which is the result of partial incorporation. This means that DVB would have one of the two alkene bonds attached to the polymer. Partial incorporation is supported by Figure 3.6 and literature reporting on water soluble polymers.²⁹

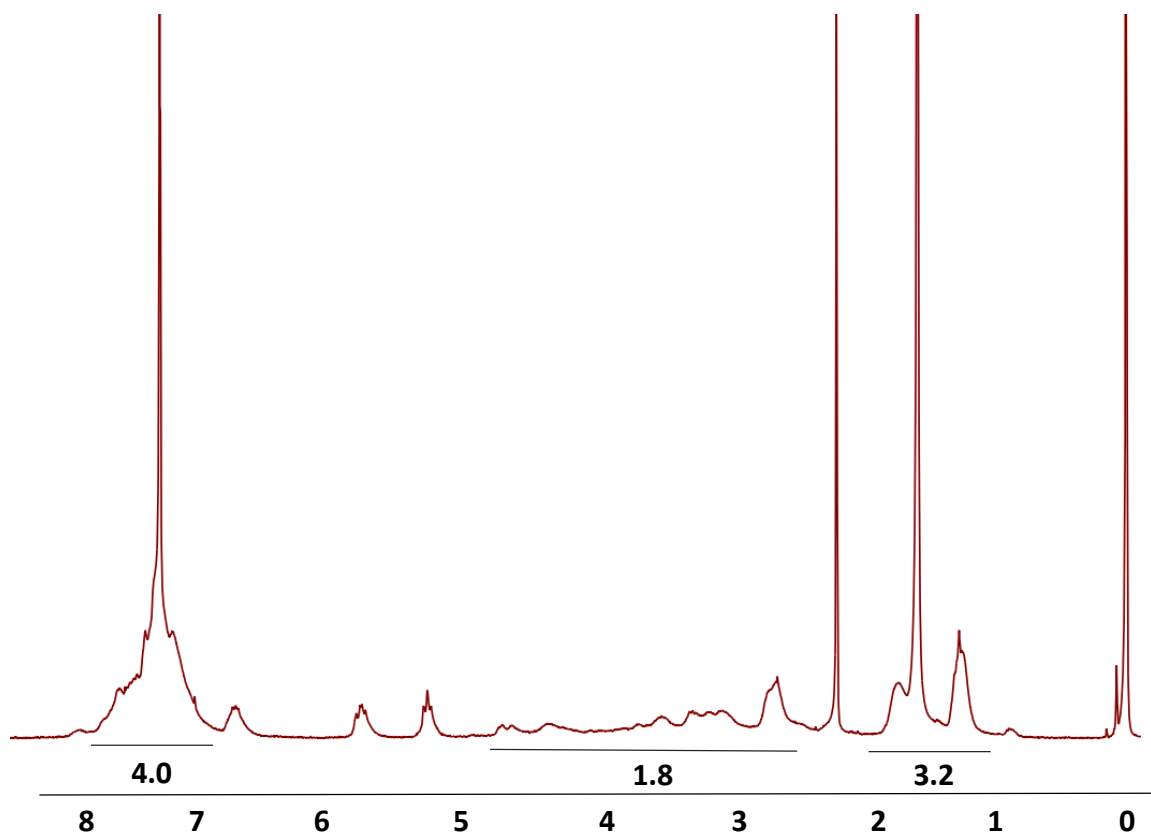


Figure 3.6: ¹H-NMR of Poly(S-DVB-DVB)

At lower poly(S-DVB):CDE ratios, 1:1 and 1:10, the incorporation of CDE is ~100% for all sulfur contents. When CDE was present in larger quantities such as a 1:50 or 1:100, poly(S-DVB):CDE, there is ~1% of unreacted CDE remaining in the sample for all sulfur contents. Although 1% monomer seems inconsequential, there was such a large amount of CDE added that unreacted monomer needed to be removed. The remaining monomer was washed out by precipitating the polymer in cold methanol multiple times until little to no monomer remained. Monomer removal can be difficult because the cross-linked matrix can trap residual monomer.

In addition to CDE, a family of monomers were chosen for their similarity in structure and functionality (allyl or vinyl, monofunctional or difunctional). The three monomers used were allyl ether (AE), cyclohexyl allyl ether (CAE), cyclohexyl vinyl ether (CVE). All had boiling points below

inverse vulcanization synthesis temperatures besides CAE (AE: 95 °C, CVE: 147 °C, and CAE 184 °C). These terpolymers were all synthesized similarly to poly(S-DVB-CDE) by adding crushed poly(S_{50%}-DVB_{50%}) and the additional monomers at a 1:1 ratio at 90 °C. The only difference was the reaction time was extended to 4 days for AE, CVE, and CAE compared to 1 day for CDE. The percent incorporation of the monomers after the 4 days was determined to be ~88% for both AE and CAE, and ~100% for CVE. The percent incorporation is logical in that allyl monomers take longer to polymerize due to the stability of radical compared to the vinyl group. NMR spectra for AE, CAE, and CVE can be found in the appendix (Figures 5.5-5.7). For the allyl monomer NMRs, the remaining unreacted monomer was removed with cold methanol.

The additional monomers, besides CDE, were forming viscous, liquid-like polymers when incorporated into poly(S-DVB). The viscosity of the terpolymer led to the belief that the poly(S-DVB) was not interacting with the additional monomers enough. To help dissolve poly(S-DVB), a high boiling point solvent, dimethylformamide (DMF), was used so that it would not boil off during the reaction. The solvent was added to poly(S-DVB) and the additional monomer and reacted at 90 °C. These samples had to undergo a workup by dissolving the polymer in CDE and precipitating it with methanol, however, DMF is incredibly difficult to remove due to the high boiling point. Despite multiple polymer precipitations, DMF solvent peaks still showed up when the sample was analyzed by NMR. The DMF was still present because with higher cross-linking, the solvent can be trapped and not easy to remove. The DMF peaks at 2.88 and 2.96 ppm overlapped with the HC-S bonds that needed to be integrated. This alteration in the synthetic procedure was determined to be too much trouble and was discarded. Figure 3.7 shows the NMR of poly(S-DVB-CVE).

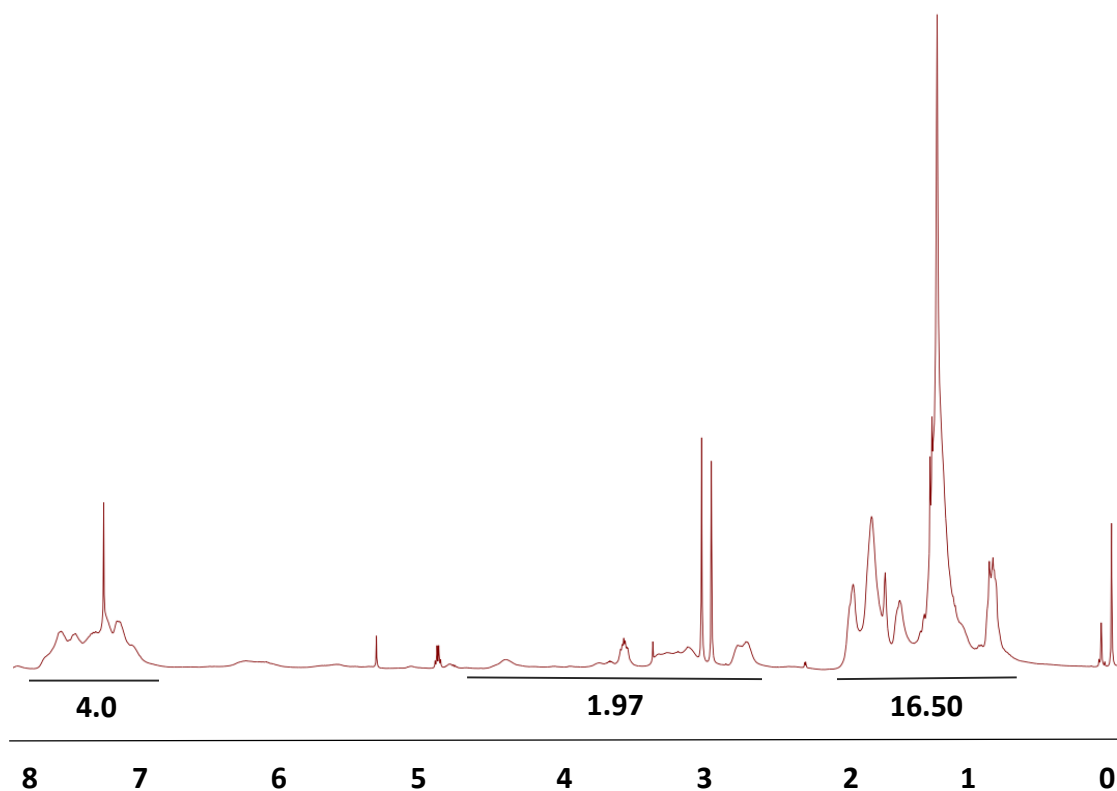


Figure 3.7: ^1H -NMR of Poly(S-DVB-CVE) with DMF Solvent

Solubility and GPC Data of Poly(S-DVB-CDE)

The solubility of poly(S-DVB-CDE) was tested to determine the cross-linking effect of including CDE. For all solubility values, concentration was kept constant at 75 mg/ 1 mL of DCM. Shown below (Figure 3.8 A) is the solubility for poly(S-DVB):CDE ratios with 50% sulfur content. As CDE content increases, the color changes from dark red to a light yellow. This is because the amount of DVB is being overwhelmed by the CDE content which reduces the intensity of the color. For the more soluble polymers, (1:1, 1:10) with 50% sulfur, the color tends to become a darker red and then changes to an orange or yellow color as the solubility decreases. The 30% sulfur poly(S-DVB-CDE) shows a darker color and the intensity decreases as the sulfur content increases to 70% sulfur (Figure 3.8 B).

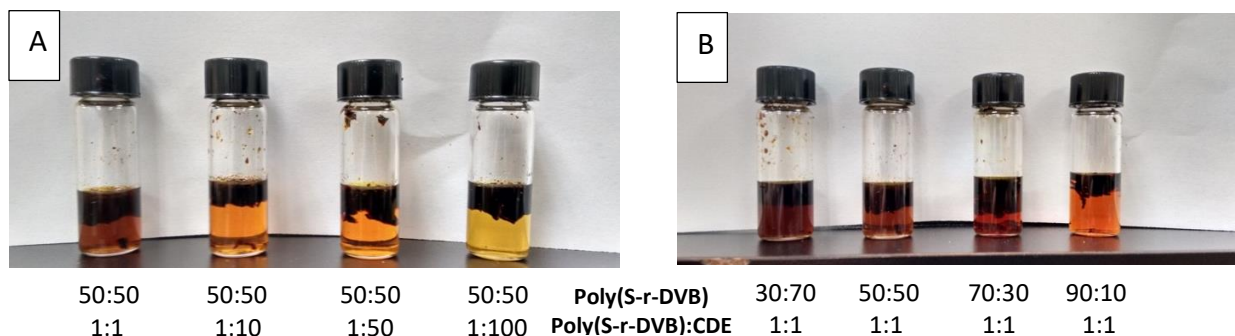


Figure 3.8 Solubility of Poly(S-DVB-CDE) with Various Poly(S-DVB):CDE

As CDE is added to 30% sulfur poly(S-DVB) forming poly(S-DVB-CDE) there is a decrease in solubility from 18% to 13%, Figure 3.9. From there, the solubility increases to 52% with the 1:10 poly(S-DVB):CDE and then steadily decreases for 1:50 and 1:100 poly(S-DVB):CDE ratios. The large increase between the 1:1 and 1:10 poly(S-DVB):CDE is clear but surprising as solubility should be decreasing with more CDE. An experiment could be conducted to determine the cross-link density of the 1:10 sample, however, the instrument is not available for analysis.

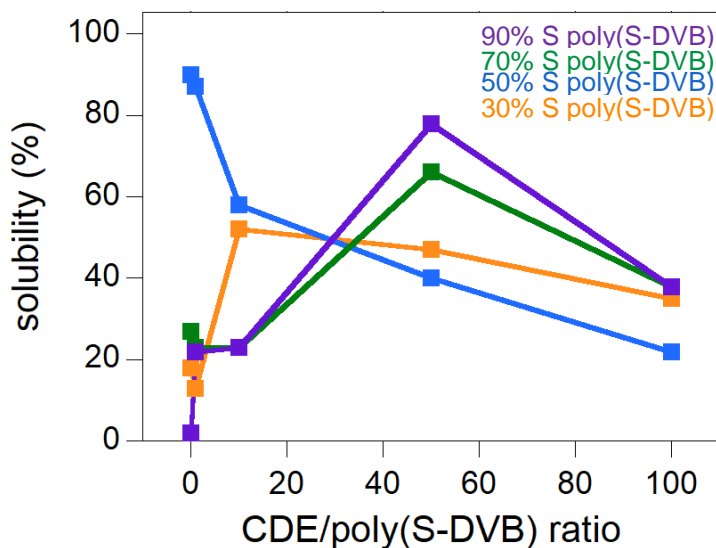


Figure 3.9: Solubility of Poly(S-DVB-CDE) for Various Sulfur Contents

The 1:1 poly(S-DVB):CDE ratio shows very similar solubility to the 50% sulfur poly(S-DVB) (87% and 90% respectively). However, the 1:10 poly(S-DVB):CDE ratio shows a large decrease in

solubility to 58% and the values steadily decrease for the 1:50 (40%) and 1:100 (22%) poly(S-DVB):CDE ratios. This is to be expected since more cross-linking should form a less soluble polymer. Reverse ratios 100:1, 50:1, and 10:1 of 50% sulfur poly(S-DVB):CDE were also studied. The range of solubility (84-92%) showed that there was no substantial difference between the starting material's solubility of 90% when small amounts of CDE are added.

When 70% sulfur poly(S-DVB-CDE) was tested (green line in Figure 3.9), there is no substantial difference in solubility for the 70% sulfur poly(S-DVB), the 1:1, and 1:10 ratios of poly(S-DVB):CDE. There is a dip in the solubility when comparing the 1:50 and 1:100 ratio values from 66% (1:50) to 47% (1:100). This is due to the interaction of the 70% sulfur poly(S-DVB) and CDE forming a gel network which would decrease the solubility.

The 90% sulfur poly(S-DVB-CDE) (purple line) shows an increase in solubility from the initial 90% sulfur poly(S-DVB)'s 2% to the 1:1 poly(S-DVB):CDE value of 22%. The low starting solubility is logical in that a very high sulfur content poly(S-DVB) is typically shown to be very insoluble.³ The 1:10 ratio shows no significant jump in solubility until it reaches the 1:50 ratio and then decreases with the 1:100 ratio. For the higher CDE content ratios, the 30, 70, and 90% sulfur samples were precipitated using cold methanol to remove any unreacted monomer. This ensured that highly soluble monomer was not contributing to the solubility of the samples.

A ratio of 1:1, 50% sulfur poly(S-DVB):DVB was used as a control. The goal was to determine how more DVB would incorporate into the prepolymer and affect the solubility. Additional DVB took much longer to incorporate, 3 days, compared to 1 day for CDE at a 1:1 ratio. The solubility of the additional DVB incorporated polymer increased from 90% for the starting material to 99%. One hypothesis is that additional DVB may be incorporating in a linear

configuration rather than just cross-linking the sample. Partial incorporation is also a factor as seen in the NMR of poly(S-DVB):DVB. The single unreacted alkene bond from DVB can contribute to higher solubility. The physical properties also showed a difference from the initial 50% sulfur poly(S-DVB). It was much harder to tear apart by hand and would audibly make a snapping sound upon pulling apart indicating more brittleness.

A 1:10 ratio of 50% sulfur poly(S-DVB):DVB was also tested and showed a color change from a dark brownish-red color to a transparent orange solid. The taffy-like initial material became a solid that could easily be broken apart by hand. The solubility of the material also showed a drastic decrease to 46% compared to 90% for the initial poly(S-DVB). This large decrease may be due to the much larger amount of DVB being incorporated into the matrix and decreasing the spacing between the branching. Furthermore, the 1:10 poly(S-DVB):DVB with 50% sulfur shows much more transparency compared to the 50% sulfur poly(S-DVB) which is opaque. This high transparency is comparable to the high transparency of the 30% sulfur poly(S-DVB).

The GPC results for poly(S-DVB-CDE) with 30% sulfur shows an increase in molecular weights as more CDE is added. Shown below (Table 3.2), there is a slight increase up to 2300 g/mol for the 1:50 ratio and then a large jump up to 6300 g/mol for the 1:100 poly(S-DVB):CDE ratio with 30% sulfur. The 1:50 and 1:100 (green line) poly(S-DVB):CDE ratios have a bimodal distribution in the elution peaks initially (Figure 3.10). There were two distinct peaks rather than just one showing there are two different populations of molecular weights in the polymer that are both very prominent. This distribution was only seen for 30% sulfur poly(S-DVB-CDE) because of the low sulfur rank in the 30% sulfur poly(S-DVB). Sulfur rank is the amount of consecutive sulfur atoms in a chain. The lower sulfur rank requires larger amounts of energy to break the S-S

bonds to reform the radicals for polymerization with CDE. To get rid of the bimodal distribution, the poly(S-DVB) was heated for 5 minutes before introducing the monomer to sufficient time to break the linear S-S bonds and reform sulfur radicals. This method was shown to be successful as only one peak would show in the GPC elution of the sample (blue line, Figure 3.10).

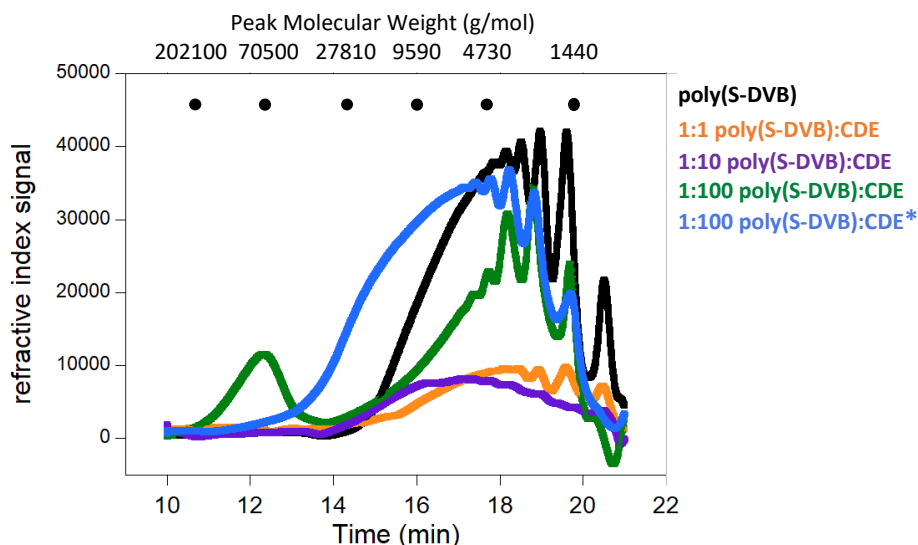


Figure 3.10: GPC Elutions of 30% Sulfur Poly(S-DVB-CDE)
The black dots indicate the various peak molecular weights of polystyrene standards.

The GPC results for 50% sulfur of 1:1 poly(S-DVB):CDE showed an initial decrease in molecular weight compared to the initial poly(S-DVB). The decrease in molecular weight is due to the amount of CDE being incorporated into poly(S-DVB). This increase in cross-linking for 1:1 poly(S-DVB):CDE does not change the solubility initially, but with more CDE content decreases the solubility. The lower solubility would then not show an overall picture of the molecular weights. Once CDE was added in larger quantities, the molecular weights began to increase. The values ranged from 1200 to 2800 g/mol (Table 3.2). This increase in molecular weight after CDE was added is logical and expected as more organic monomer with the same number of radical

initiators should increase the molecular weights. The 70% poly(S-DVB-CDE) showed an increase in molecular weight as the amount of CDE increased, much like the other sulfur contents of 30 and 50% sulfur poly(S-DVB-CDE), (Table 3.2). The molecular weight increase is logical in that more monomer incorporation gives higher molecular weights.

Table 3.2: GPC of Poly(S-DVB-CDE) with Various Sulfur Content

S:DVB	Poly(S-DVB):CDE	M _w	S:DVB	Poly(S-DVB):CDE	M _w	S:DVB	Poly(S-DVB):CDE)	M _w
30:70	1:0	2700	50:50	1:0	3700	70:30	1:0	-
	1:1	1600		1:1	1200		1:1	700
	1:10	2400		1:10	1100		1:10	1700
	1:50	2300		1:50	1900		1:50	2100
	1:100	6300		1:100	2800		1:100	3400

The 24 hour reheated poly(S-DVB) control showed no substantial change in molecular weight (3700 g/mol) compared to the initial starting material's value (3600 g/mol), Table 3.3. Despite the limited difference in molecular weight, there may have been a rearrangement of monomer and sulfur chains since the NMR integration values change from a HC-S:HC-C ratio of ~1.0:1.0 to ~1.0:1.3 after heating the poly(S-DVB) for 24 hours.

When the poly(S-DVB) was heated with more DVB at a 1:1 ratio, the molecular weight reached a very high value at 131,500 g/mol. The elution peaks were very wide indicating a high PDI and showed a large amount of tapering off at the end towards the higher molecular weight side (Figure 3.11, blue line). This large molecular weight was the result of partial incorporation occurring over the 3-day reaction. The apex of the elution is where the highest population of chains are, otherwise known as the peak molecular weight (M_p). For the 1:1 poly(S-DVB):DVB,

the M_p value was 8900 g/mol. It was much less than the initial integrated value of 131,500 g/mol, but larger than the initial starting material's molecular weight of 3700 g/mol. The solubility difference between the two was very small, so solubility did not play a major role in the overall molecular weight difference.

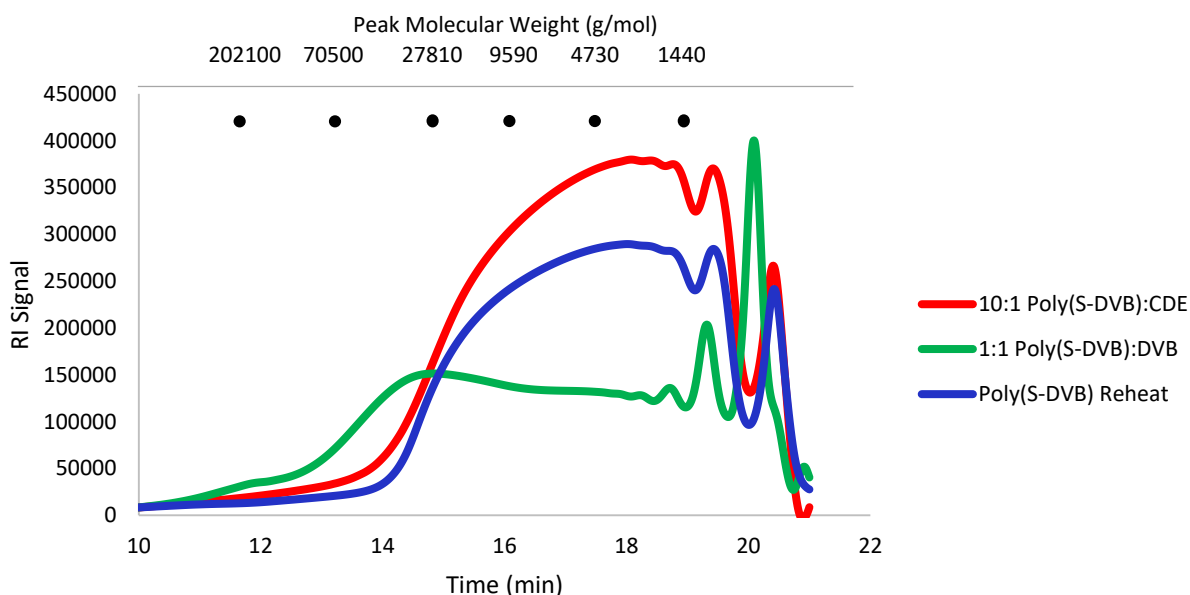


Figure 3.11: GPC Elutions of Tapered Poly(S-DVB) Terpolymers
The black dots indicate the various peak molecular weights of polystyrene standards.

A small subset of poly(S-DVB):CDE control ratios were synthesized with reverse ratios (100:1, 50:1, 10:1) where the amount of poly(S-DVB) was much greater than the amount of CDE being incorporated. There was a difference in how the elution peaks appeared in the GPC as there was a tapering of the curve toward the higher molecular weight region. Figure 3.11 shows the tapered sample of 10:1 poly(S-DVB):CDE with 50% sulfur (red line). The graph shows a large difference around the 10-14 minute mark for both the poly(S-DVB) reheated sample (blue line)

and the 1:1 poly(S-DVB):DVB sample (green line). Table 3.3 shows the molecular weights of these ratios.

Table 3.3: GPC of Controls and Poly(S-DVB):CDE Reverse Ratios

S:DVB	Poly(S-DVB):CDE	M _w (g/mol)
50:50	1:0	3700
	1:0 (reheat)	3600
	1:1 (DVB)	131500
	100:1	4200*
	50:1	4800*
	10:1	6800*

*High molecular weight tapering observed

Physical Properties and DSC of Poly(S-DVB-CDE)

The monomer 1,4-cyclohexanedimethanol divinyl ether, CDE, is a dynamic monomer. The cyclohexane ring allows free rotation about the bonds and can change the characteristics of poly(S-DVB). Furthermore, the terpolymer, poly(S-DVB-CDE) has very different physical properties than poly(S-DVB). The addition of CDE produces a very tough and rubbery material. It cannot be torn apart by hand but requires a razor blade to cut it apart. The cross-linking of the polymer likely contributes to the rubber-like properties. The higher ratios (1:50-1:100) poly(S-DVB):CDE for all sulfur contents forms the black gel that also is very sticky and adheres to anything it comes into contact with.

All poly(S-DVB-CDE) samples were examined by DSC. As CDE was added, samples showed a general decrease in T_g for all sulfur contents (Table 3.4). The T_g is decreasing due to poly(S-DVB-

CDE) having higher quantities of CDE. The cyclohexane ring in CDE is very flexible due to the single bond rotation providing a large free volume, so poly(S-DVB-CDE) can move more freely than poly(S-DVB). Poly(S-DVB) is very stable and rigid due to the aromatic ring. There is limited rotation with DVB. The DVB matrix offers a decrease in free volume making it difficult for the polymer chains to flow freely past one another at lower temperatures.

Table 3.4: T_g Data of Poly(S-DVB-CDE) with Various Sulfur Content

S:DVB	Poly(S-DVB):CDE	T _g (°C)	S:DVB	Poly(S-DVB):CDE	T _g (°C)	S:DVB	Poly(S-DVB):CDE	T _g (°C)
30:70	1:0	74	50:50	1:0	52	70:30	1:0	28
	1:1	45		1:1	14		1:1	28
	1:10	1		1:10	31		1:10	11
	1:50	-6		1:50	10		1:50	2
	1:100	-		1:100	9		1:100	8

Figure 3.12 shows the thermograms of 50% sulfur poly(S-DVB-CDE). The various ratios of 50% show a jump up in the T_g at the 1:10 ratio (red) to 31 °C from 14 °C for the 1:1 ratio (dark blue). The interaction with the poly(S-DVB) and CDE creates a more thermally stable polymer matrix than the other ratios. This is not expected because CDE at higher quantities would be expected to form materials with high free volume. Why the 1:10 poly(S-DVB):CDE ratio has a larger T_g than the 1:1 may be due to the abnormal high amount of HC-C bonding that is occurring in the 1:10 sample compared to the 1:1 ratio.

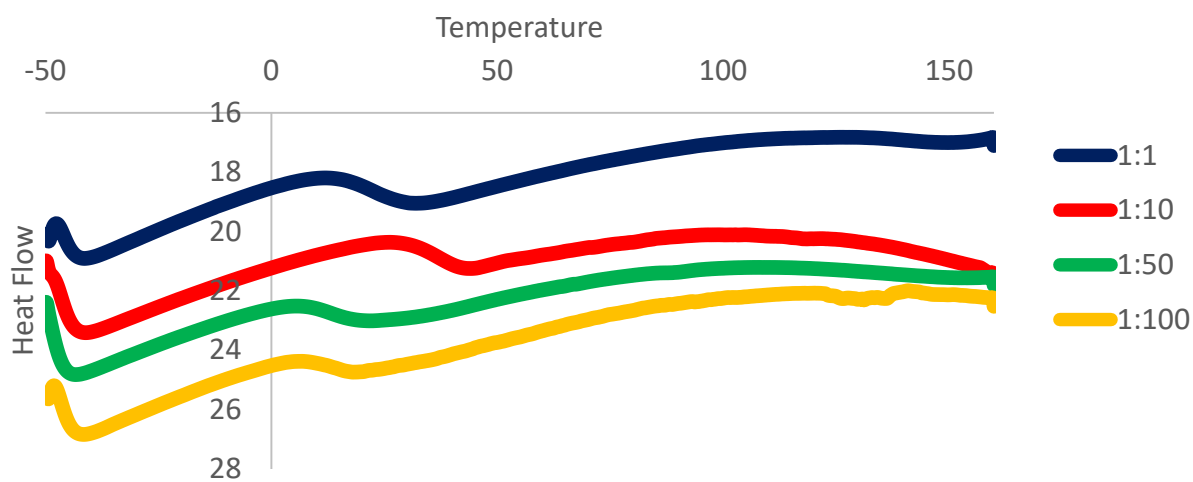


Figure 3.12: Thermograms of 50% Sulfur Poly(S-DVB):CDE Ratios

CHAPTER 4: METAL BINDING OF POLY(S-DVB):ADDITIONAL MONOMER

Metal Binding of Poly(S-DVB-CDE)

Preliminary metal binding results were obtained to determine how CDE can affect the metal binding characteristics of poly(S-DVB). The inspiration for the metal binding experiments stems from the previous literature using poly(S-DIB), and poly(S-Limonene) which were both successful at binding to mercury ions in water. Poly(S-DVB) and CDE were combined to form the terpolymer, poly(S-DVB-CDE) for the use in metal binding studies. Fe and Cu metal ions were chosen because of their ability to bind well to sulfur.³⁰ Lack of research with these metals in inverse vulcanized polymers as well as their less toxic nature compared to Hg and Pb metal ions also promoted their use.

Using hydrated salts, $\text{FeCl}_2 \bullet 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \bullet 2\text{H}_2\text{O}$, poly(S-DVB-CDE), poly(S-DVB-CVE), and poly(S-DVB-AE) were exposed to a concentration of $(2.45 \times 10^{-4}\text{M})$ of FeCl_2 and CuCl_2 solution for 24 hours. All terpolymers were exposed to the solution in a glass vial and para-filmed to prevent evaporation. Any evaporation of the water could alter the concentration of the solution for analysis. The flame atomic absorption spectrometer (Flame-AA) was used to analyze the metal concentration in the samples after exposure to the polymer. Standard solutions diluted from the initial solution were used to create a calibration curve. The concentration of the final solution, after interacting with the polymer was determined from the calibration curve. The values that are obtained are in units of mg of either Fe or Cu per gram of polymer.

Figure 4.1 shows the how much Fe and Cu ions were absorbed by the terpolymers. All terpolymers were better at binding Fe than Cu. Both vinyl monomers, CDE and CVE, were more successful at binding to Fe than AE. A control was conducted for both iron and copper solutions

in to determine if the glass vials were capturing metal ions. The glass vials could bind to some metal ions, however, the terpolymers were capturing substantially more iron or copper. The values that were obtained with Cu binding are comparable to published literature binding to thioether-functionalized polymers.³⁰ The copper binding values they obtained were between 0.6-1.8 mg Cu/ g of polymer for various concentrations of Cu (2-10 ppm).³⁰

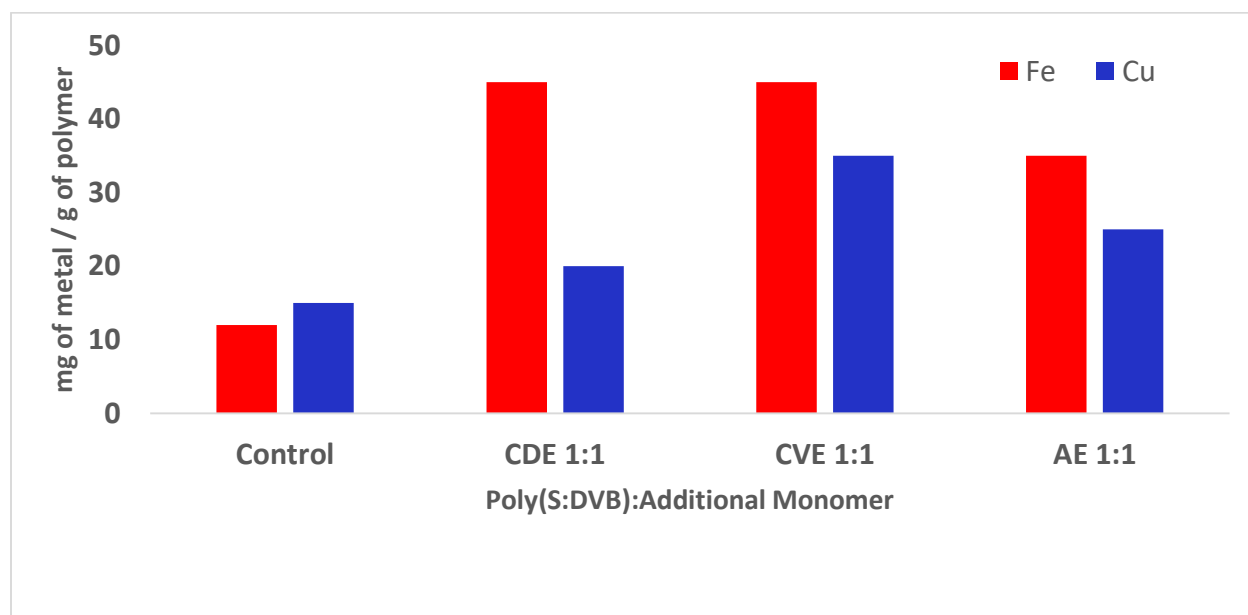


Figure 4.1: Metal Binding of Various Terpolymers with Fe and Cu

Zinc ions were also tested with the terpolymers due to its ability to bond with sulfur which is well known in enzyme biochemistry.³¹ Zn was also chosen as it was related to a local issue at a water plant. Industrial waste is being treated for a toxic anion. Although the remaining zinc concentrations are safe, high contents would clog water filters. However, zinc was very difficult to work with in terms of analysis. The flame-AA had problems with analyzing the solution in that the zinc ions would clog the inlet tube which would prevent the spectrometer from accurately reading the solution's absorbance. For the data that was obtained, it showed that zinc did not

bind well to the polymer. Various trials were conducted to determine if zinc binding could be improved, but the results that were given showed little to no binding.

Swelling of poly(S-DVB-CDE) was studied to determine how CDE can affect the swelling characteristics of the polymer. The swelling data could then possibly explain the metal binding data. The more the polymer could swell, then the polymer should in theory be more porous for metal ions to travel through the matrix and bind to sulfur atoms. All poly(S-DVB-CDE) samples were exposed to 2 mL of water for 24 hours. The samples were removed from the water after and the mass was recorded. All polymers had some degree of swelling. However, there was no discernible logic behind the values. The values would jump from a low percent value and then jump to a high value and then decrease again. The data that was gathered showed no real connection to the metal binding data. In theory, the more cross-linking in polymers, the more swelling that the polymer should have. However, this is not what is being observed. The swelling of all poly(S-DVB-CDE) terpolymers is still being tested to determine more reliable results.

There were several characteristics that the polymers did show however while exposed to the water. The polymers were changing color while exposed in the solution. There were two noticeable colors observed which were a light tan/sawdust color and a dull light gray color. The appearance of ridges in the polymer surface were also noticed. It remains to be seen if the ridges were there initially in the polymer before being exposed to water, but the water may enhance their appearance revealing surface qualities not able to be seen by the naked eye.

CHAPTER 5: CONCLUSIONS

Poly(S-DVB) was synthesized and all of the characterization values from NMR, GPC, and DSC showed similar results to published literature. The synthesis of the poly(S-DVB-CDE) terpolymer shows an improvement on the inverse vulcanization technique by lowering the temperature from 185 °C to 90 °C. This large span in temperature allows the use of a variety of monomers to be incorporated into copolymers. Lower boiling point monomers with different functionality such as allyl and vinyl (mono or difunctional) can be incorporated successfully at lower temperatures than previously reported. Poly(S-DVB) in small amounts can be used to initiate a copolymerization with CDE at various poly(S-DVB):CDE ratios.

The characterization methods of poly(S-DVB-CDE) show that the inclusion of additional monomer can change the initial starting material, poly(S-DVB). Solubility of copolymers can be tailored by the inclusion of additional monomers. This is seen by the incorporation of CDE by decreasing the solubility with increasing CDE content. Molecular weights of copolymers can be increased or decreased by the addition of another monomer which is observed with CDE increasing the molecular weights at higher quantities. Material properties of poly(S-DVB) can be changed with the incorporation of additional monomers by lowering the glass transition temperatures with increasing additional monomer content due to the flexible CDE monomer. Other additional monomers can be used to raise or lower glass transition temperatures depending on the role of the terpolymer. Preliminary metal capture data for all terpolymers used [poly(S-DVB-AE), poly(S-DVB-CVE), poly(S-DVB-CDE)] shows a higher Fe binding compared to Cu. The Cu binding efficiency of poly(S-DVB-CDE) is comparable to published literature with a different sulfur-based polymer. Ultimately the synthesis of poly(S-DVB-CDE) and other additional

terpolymers shows an improvement in polymer chemistry by introducing a novel modification to inverse vulcanization. This allows the synthesis of tailored terpolymers for a specific role.

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APPENDIX

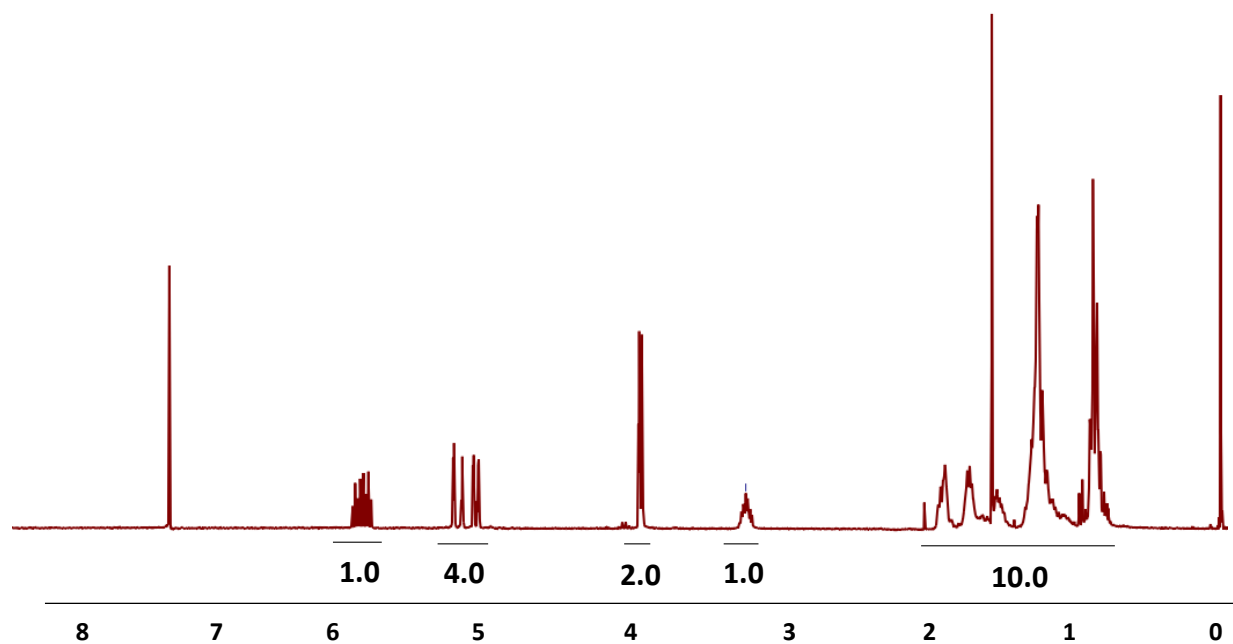


Figure 5.1: ^1H -NMR of Cyclohexyl Allyl Ether

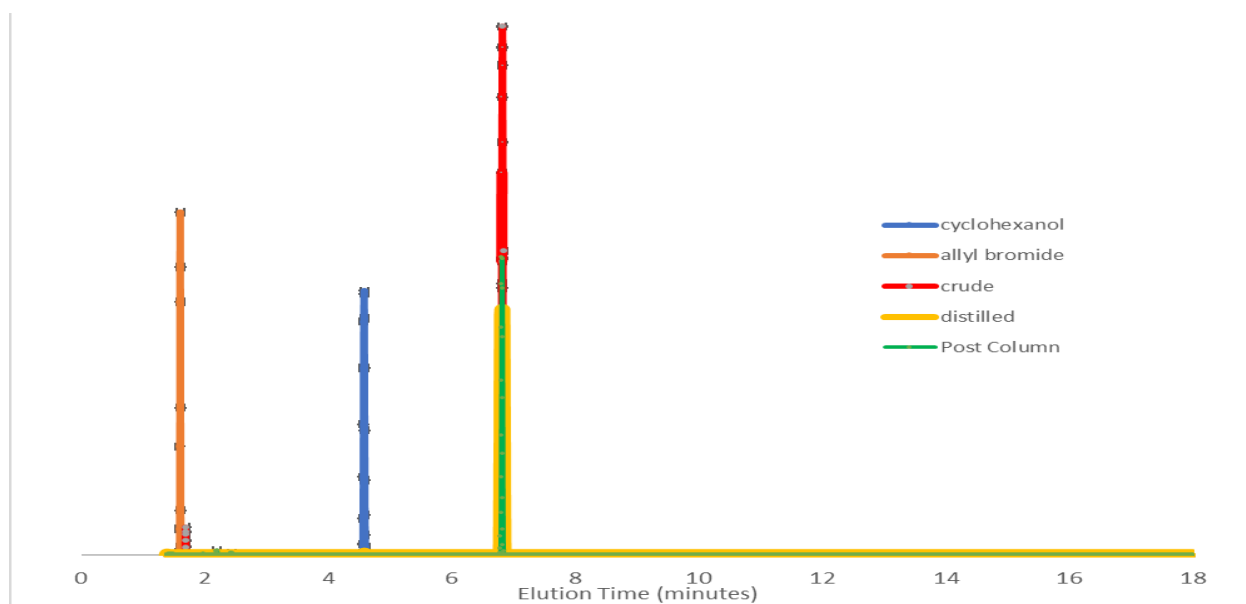


Figure 5.2: Gas Chromatogram of Cyclohexyl Allyl Ether

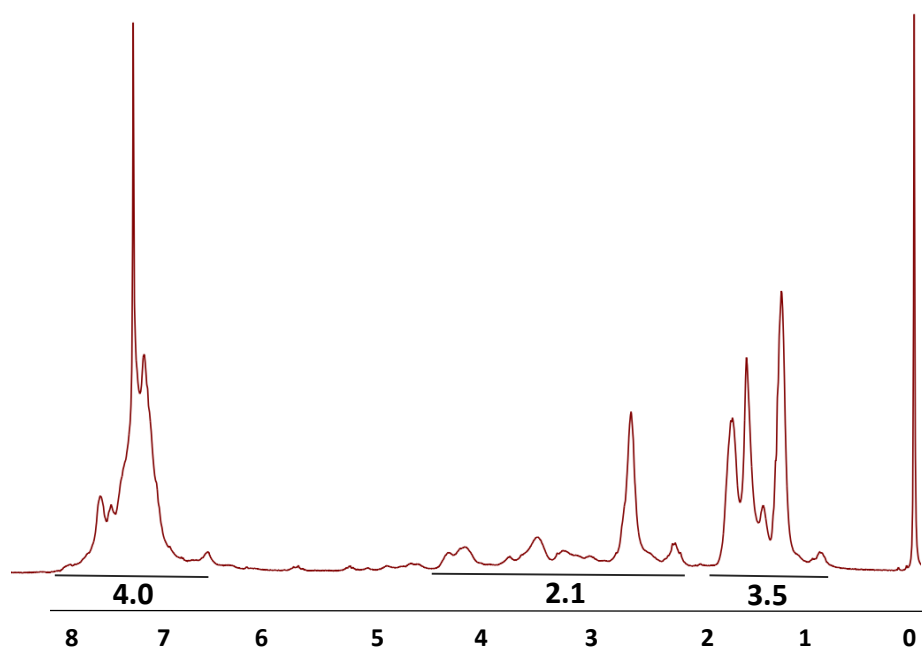


Figure 5.3: ^1H -NMR of 30% Sulfur Poly(S-DVB)

HC-S : HC-C = 1 : 1.7

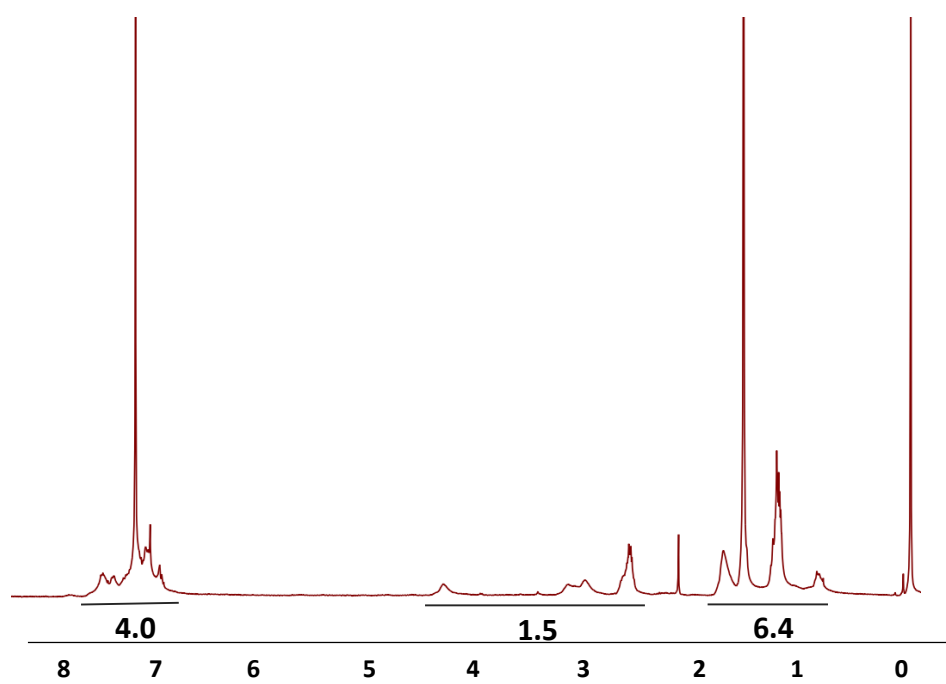


Figure 5.4: ^1H -NMR of 70% Sulfur Poly(S-DVB)

HC-S : HC-C = 1 : 4.2

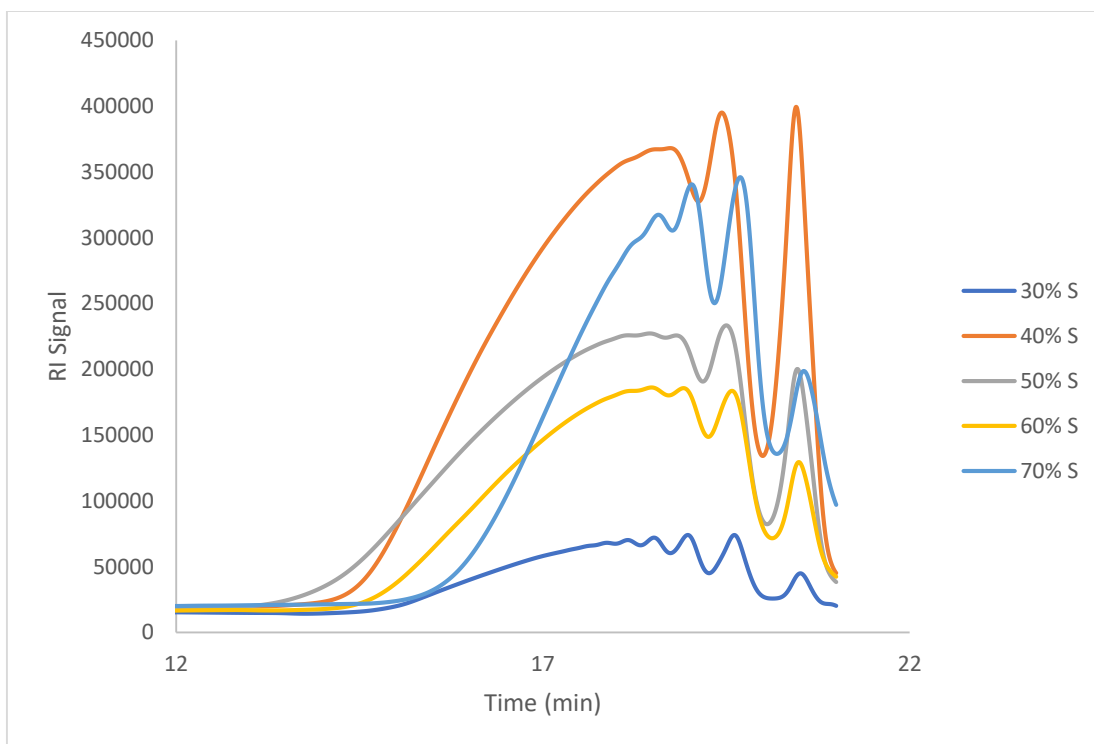


Figure 5.4: GPC Elutions of Poly(S-DVB) with Varied Sulfur Contents

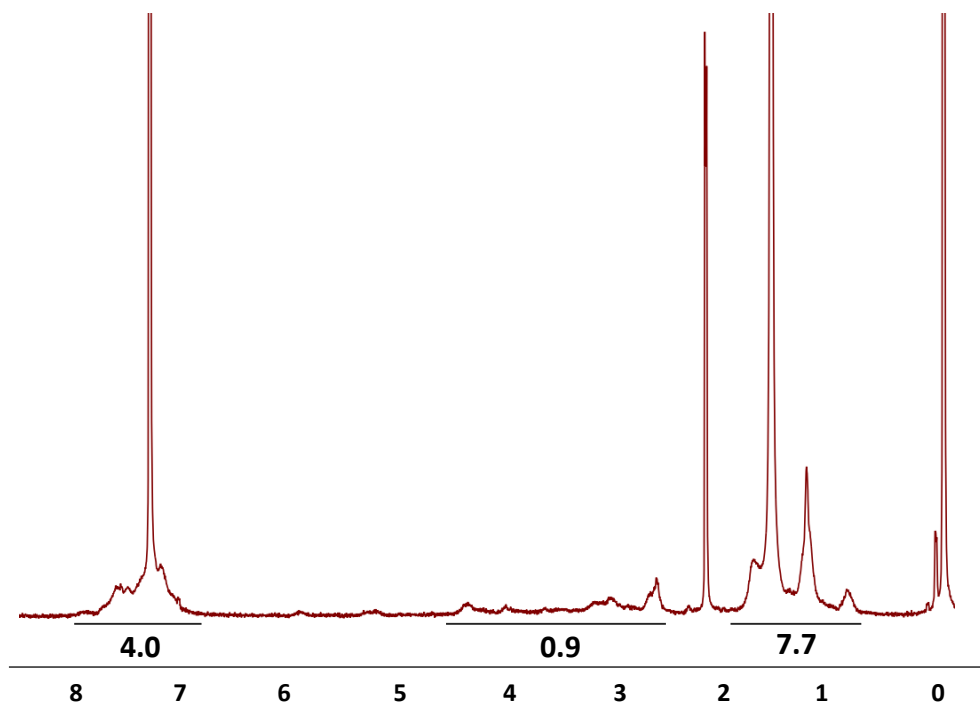


Figure 5.5: ^1H -NMR of Poly(S-DVB-AE)

HC-S : HC-C = 1 : 8.4

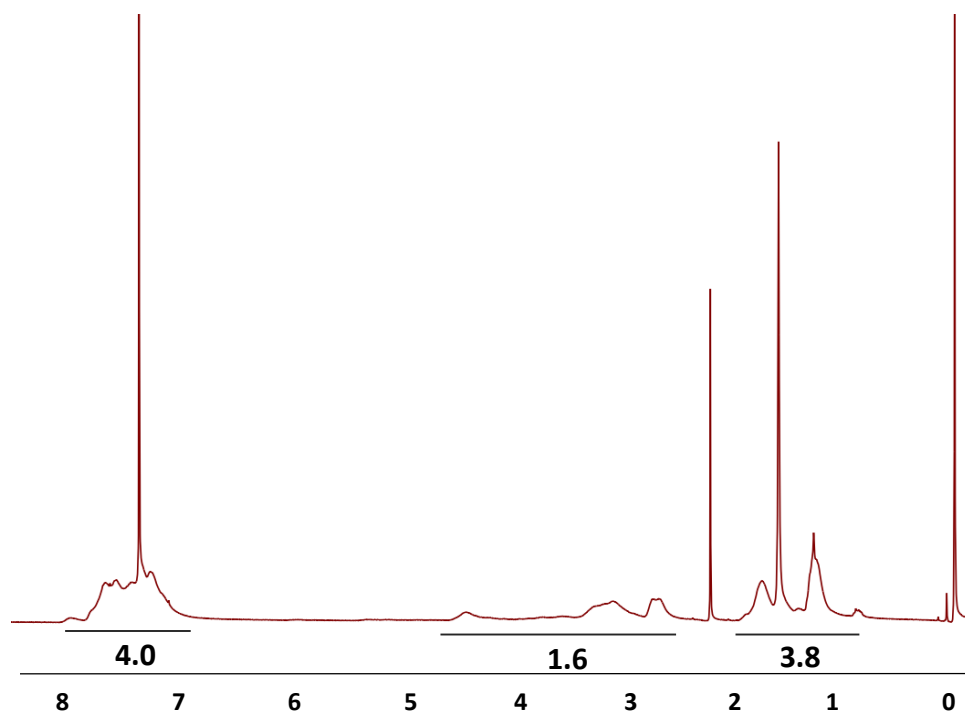


Figure 5.6: ^1H -NMR of Poly(S-DVB-CAE)

HC-S : HC-C = 1 : 2.3

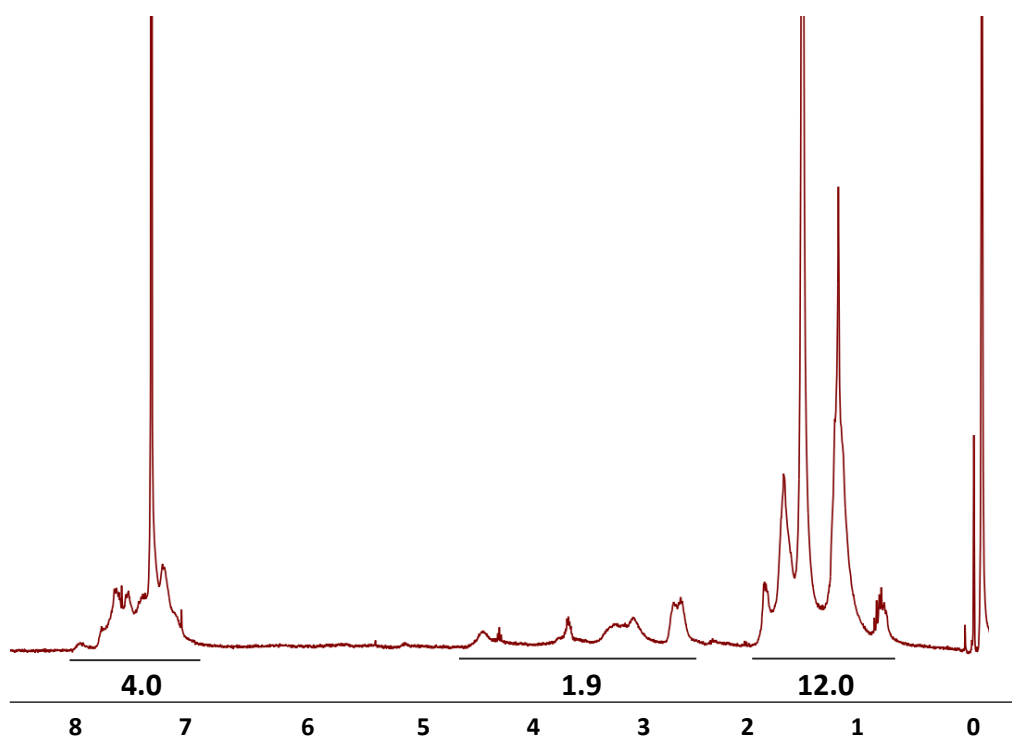


Figure 5.7: ^1H -NMR of Poly(S-DVB-CVE)

HC-S : HC-C = 1 : 6.0